We are very grateful to the two reviewers for their helpful observations, comments, and suggestions.

In the following file, please find a point-by-point response to the reviews and the reviewed version of the manuscript with changes marked-up.

Referee #1

Interactive comment on "Composition and Vertical Flux of Particulate Organic Matter to the Oxygen Minimum Zone of the Central Baltic Sea: Impact of a sporadic North Sea inflow"

by Carolina Cisternas-Novoa

Anonymous Referee #1 Received and published: 19 September 2018

The authors demonstrate their investigations of particulate matter in the water column and in sediment traps in two basins (Gotland Basin (GB) and Landsort Deep (LD)) to estimate its composition and the particle flux in theses basins and how it changes dependent if the deep water is oxygenated or not. Thus, the manuscript can be a significant contribution to understand the biogeochemical processes and its spatial variation in the Baltic Sea. However, the ms is difficult to read and to get a 'take home massage' because it contains many nonspecific verbalization. For example, it is often unclear which depth horizons are meant or why the situation at a certain depth is mentioned at this place (e.g. 110m in line 31).

The influence of the MPI must be presented more clearly and substantiated. This requires comparison of a defined depth range which is oxygen rich in one basin and low in oxygen in the other. In the GB, the situation after MBI should be compared with a situation during a stagnation period, if possible. Many of these things are present in the ms but not clearly and focused demonstrated. I would expect from the title what is transported from the overlaying layers to the OMZ. Indeed, data for the whole water column of the GB and up to 200m in the LD are given without any Accentuations.

Abstract: The objectives are not clear Line 17-18: "Oxygen (O2) depletion may improve the efficiency of the biological carbon pump". Is this sentence the hypothesis of the work? If yes, than it has to be indicated and it needs to be answered at the end of the abstract.

AR: We will add information to the abstract, about the oxygen conditions at each depth where we deployed a sediment trap in GB and LD (ex: oxygenated surface, the core of the oxygen minimum zone and deep water oxygenated by the inflow) to clarify why we mention specific depths.

We explicitly add the hypothesis and rephrase the objectives for clarity. We answered the hypothesis at the end of the abstract when we expose the differences in POM and export between the two studied stations, and we propose a mechanism to explain those differences.

Information about oxygen conditions at depths where sediment traps were deployed in each station was added in L22-25. We explicitly add the hypothesis to the abstract (L25-27)

Line 20-21: I would replace "Major Baltic Inflow "by" salt water inflow" here.

AR: This was change to "a major oxygen-rich saltwater inflow" (L21)

Line 24-32: It is difficult to understand what the comparison of the two depths means for the task.

AR: This paragraph was modified for clarity and as mentioned above, the oxygen conditions at each depth are mentioned (ex: oxygenated surface, the core of the oxygen minimum zone and deep water oxygenated by the inflow)

Line 29: Why "contrastingly"? POC and PN decreased too.

AR: We agree this was confusing "contrastingly" was deleted

Line 33: why "may form"? I think it is a result of this work.

AR: We said "may form" because, as we explain in the next line, our results suggest that MnOx-like particles aggregate with POM, this is what we propose. However, we think that to ensure that MnOx and POM aggregate and the specific composition of those aggregates, we will need to investigate aggregate formation and composition further.

Line 38: sink instead of sank

AR: This has been fixed.

Introduction:

Line 78-80: " . . ..(Tamelander et al. 2017)". Please replace "On the long term, a decrease in OM downward flux may limit the oxygen depletion." By "The reduction of nutrient inputs as target by HELCOM can cause a decrease in OM downward flux and limit the oxygen depletion."

AR: The sentence has been replaced according to the reviewer suggestion.

Line79-80. I would delete the last sentence of the chapter.

AR: The last sentence of the paragraph "However, to fully suppress hypoxia enhanced ventilation would be necessary the bottom waters of the Baltic Sea" is to emphasize that the bottom-water oxygen concentrations, are not only controlled by the nutrient loads, but also by physical factors like the frequency and intensity of the saltier water inflow, which had a decadal variability and it is modulated by meteorological forcing (e.g., Carstensen et al. 2014). This is explained in the next paragraph.

Line 88: ". . . Carstensen et al. 2014)". Recommendation: Salt water inflows from the North Sea. . .. . .

AR: The sentence has been modified according to the reviewer recommendation.

Line 91-92 "Saltier, denser, O2-rich North Sea waters entered the western Baltic Sea in December 2014 and reached the Gotland Basin on February 2015." The sentence could be deleted.

Line 92-95: "At the time of sampling, this MBI also affected the neighboring Faroe Deep; but not the LD, located further northwest. The sentence can be deleted.

AR: We modified this paragraph and combined those sentences as "At the time of sampling, this MBI had reached the Gotland Basin, but did not affect the LD, located further northwest." to emphasize that the MBI oxygenated the deep waters of GB, but not those of LD (L97-98).

Line 100: Please add the water depth in which the redox lines occur.

AR: We added the redoxcline depth from literature (between 120 and 150 m depth; L102). In the results, we define the redoxcline depth determined from the O2 and H2S concentrations during our sampling.

Line 99-100: This chapter can be shortened and combined with the chapter before.

AR: We think that provide background information on the chemical reactions occurring in the redoxcline, and how previous MBI had altered redox conditions, is important to frame our idea that changes in oxygenation enhance the formation of MnOx that aggregate with POM and alter POM distribution and export

Line 118-119: "enriched with OM; specifically with transparent exopolymer particles".

AR: This has been fixed (L122).

Line 134-142: A clear objective is missing here.

AR: This paragraph has been modified to clarify the objectives of the study (L138-146)

Methods

Line 146: "surface-tethered sediment traps"that's not true. Traps were also installed in 180 m

AR: As explained in the section "Sediment trap design and deployment"(L158-164) and in more detail in Engel et al. 2017 and Knauer et al. 1979, our traps consisted of 12 particle interceptor tubes (PITs) framed in five PVC crosses. Crosses with PITs tubes are attached at four depths: 2 at 40m, 60m, 110m, and 180m. The entire array is attached to the flotation gear that consists on a polypropylene line attached to two different types of flotation spheres. The entire flotation array is secured to the surface spar (a large yellow buoy) on which the flashlight and positioning systems are mounted.

Line 147-148: depth of water sampling should be given here.

AR: Water sampling depths are in table 2; this was added to the text (L152)

Line 150: conductivity temperature depth? Suggestion: Temperature, salinity and O2 concentration were determined at each station using a Sea-Bird (CTD) probe equipped with a oxygen (Oxyguard, PreSens) sensor that was calibrated. . .

AR: This paragraph has been modified according to the reviewer recommendations (L153-154)

Line 155: According to Table 1, there are 3 or 4 depths in which the traps were exposed. That should be mentioned here as well.

AR: The sediment trap depths were added to the text (L158).

Line 174-178: Ammonium has to be measured in an unfiltered sample. However if samples for nutrient analysis are stored frozen and analyzed using an auto-analyzer, then filtration is necessary. Please correct.

AR: We thank the reviewer for this observation. The paragraph was corrected (L176-181).

Line 191-192: Please add the wave lengths

AR: The wavelengths were added to the text (440/685 nm; L195)

Line 215-219: Suggestion: ”Particle number and area was measured semiautomatically using an image analysis system including the WCIF ImageJ software. Image analysis of TEP and CSP were and conducted after Engel (2009). Additionally, TEP and CSP in water samples from the stations where we deployed sediment traps were analysed spectrophotometrically according to Passow and Alldredge (1995) and CisternasâA˘ RNovoa et al. (2014) respectively. Why was the additional method ap- ˘ plied?

AR: We modified the sentence according to the reviewer suggestion (L219-222). The additional spectrophotometrically method was used to measured TEP and CSP concentration in the water column. Since the spectrophotometric method is less labor intensive, it allows for sampling of the water column with higher vertical resolution (between 9 and 12 depths; L223)

Line 223: For TEP and CSP it should be mentioned that the red and the green channel were used?. Here should only be mentioned that the blue channel was used.

AR: We modified the TEP, CSP (L219-222) and MnOx (L230-232) image analysis section according to the reviewer suggestion.

Line 226 and line 233: Please delete the word ”directly”. When storing samples, there is no direct measurement.

AR: We deleted the word “directly”

Results Generally: I suggest that the results should be demonstrated for the basins successively (at first for the GB and after it for the LD) and not switched between the basins. In the vertical direction it should be started with the surface then successively the deeper layers whereby the depth of each layer should be defined to understand the results reported thereafter. Information about temperature and salinity is missing in the text.

Line 250-251: Information about the thermocline should be moved to the beginning of the chapter. The traps were exposed for one or two days. The water samples were taken at the same time. I don’t believe that there was such a large rage where the thermocline was located during this short time.

AR: The organization of this paragraph was changed according to the reviewer suggestion, i.e. Temperature, salinity and O_2 conditions were discussed first in GB and then in LD. Information about temperature and salinity were added to the text. We include the thermocline information

based on the measurements made during the deployment of the sediment traps. The depth range presented correspond to the initial and end depth were the temperature had a rapid decreased, this information was added to the text.

Line 259: Which depth is meant with surface water?

AR: We added to the text that surface water mean upper 10 m.

Line 260: Suggestion for changes: (6 µM at 80 and 140 m, and 0.12 260 µM at 110 m). It could be added already here that the upper (80m) and lower (140m) bounds and 110m the core of the OMZ are. It is mentioned later, but it should be already included here.

AR: We added the information about upper, lower oxycline and OMZ core in this sentence (L278-279).

Line 270: Because the conditions in water column are reported, it should be mentioned that nitrite had a maximum at 370m (Fig.2).

AR: We added the maximum of nitrite at 250 m and nitrate at 400 m to the text (L291-292)

Line 273-274: To which depth the second nutrient values apply; "the upper 110m" is confusing here.

Line 275: 0.22µM?

Line 269-276: The individual nutrients should be described one after the other and not switch between them several times.

AR: We modified the nutrient section for clarity

Line 285: Please insert some data.

Line 286: Do you mean the sum of pico- and nanophytoplankton?

Line 287-288: 92% of what? Recommentation: Picocyanobacteria determined by phycoerythrinfluorescence amounted 92% in GB and 96% in LB of the total picophytoplankton and was 30% . . ...

AR: We modified this paragraph according to the reviewer suggestion (L310-311)

Line 289: "The abundance of larger phytoplankton (>5µm) was determined by microscopy". The sentence can be deleted. It is described in the methods.

AR: This sentence was modified (L313)

Line 293: Filamentous unicellular cyanobacteria. A cyanobacteria filament always consists of more than one cell.

A: We thank the reviewer for this observation, "unicellular" was deleted

Line 292-293: “Cyanobacteria were 60% less abundant in the GB than in the LD.” It is mentioned 2 sentences before. It can be deleted here.

AR: We deleted this sentence

Line 297: 95% of what

AR: We changed the sentence to “were more abundant in the GB than in LD (25% and 4% of the total phytoplankton respectively)”

Line 302: which layer is meant with the surface.

AR: With surface we referred to the upper 10 m of the water column. This was added to the text.

Line 316: . . ..decreased quickly at 10m. . .” Rather: . . .decreased quickly below 10m. . ..

AR: We thank the reviewer for this observation, the sentence was fixed

Line 318: The units of TEP and CSP should be explained in the methods.

AR: We add the units for TEP and CSP to the method section (L225-228)

Line 324: “. . .were only observed. . .” instead of “. . ..were observed. . .”

AR: This has been modified.

Line 331: What is ESD? Please give the full name.

AR: We added equivalent spherical diameter to the text

Line 341: “POC flux slightly increased by 18% from the shallowest (40 m) to the deepest (180 m) depth. Fluxes of PN and CSP were higher at 40 and 60 m and decreased by 19 and 70% from 60 to 180 m.. . .”. I assume the layers 0-40m and 0-180m are meant.

AR: Yes, since we collected discrete samples at 40, 60, 110 and 180m, the assumption is that at each depth the sediment trap collected the particles formed and sinking from the euphotic zone.

Line 356: “. . ..sediment traps at 110 m and 180 m. MnOx- like were They occurred as single particles and forming formed . . ... and with other particles. . .. ”.

AR: This has been modified.

Line 361: “. . ...ranged from 0.6 to 16.5 mm (media mean 1.8) at 110 m (Table 4).

AR: We referred to the “median” as a measure of central tendency. The word “median” was fixed in the text

Line 371-381: These chapters would be easier to understand if data are inserted.

AR: We added the POC: PN ratio range to make the paragraph easier to follow.

Line 390: Please indicate in the method chapter how the DI has been calculated.

AR: We added the DI calculation to the method section (L240-244)

Line 300-401: “We assess the potential influence of increased O2 concentration caused by the 2014/2015 MBI in the GB on the chemical composition and degradation stage of the sinking and suspended OM relative to the anoxic LD.” In my view, this is not clear enough in the ms, including the discussion.

Discussion The discussion involves a lot of repetition of the results.

Line 404-405 "...primary production“. Do you mean phytoplankton biomass? PP measurements were not included in this study.

AR: We replaced PP by phytoplankton biomass

Line 410-411: ”Pico-phytoplankton cell abundance (cell mL-1) dominated the small phytoplankton size fraction < 5µm (Table 2), suggesting a significant contribution to PP and Chl a concentration. This can not be deduced from the abundance alone.

AR: We deleted the sentence “suggesting a significant contribution to PP and Chl a concentration”

Line 421-422: “Cell abundance of total phytoplankton (>5 µm) were not significantly different (p=0.74) in the GB and the LD.” Which phytoplankton group refers to this statement. According to Table 3 the cell counts in both basins differed. I am wondering that the differences are not significant.

AR: To determine if the total phytoplankton abundances (considering all groups presented in table 3) were significantly different we used the Mann-Whitney U-test. The p-value (0.74) indicates that there is not sufficient evidence to indicate that the medians of those two data set were significantly different.

Line 434: “Our samples were collected right after the peak of the spring bloom. . ...”. That is not right. The spring bloom occurs, for example in the Gotland Basin, from the middle until the end of April (see also publications by B. Schneider et al.). The investigations were carried out in June.

AR: We corrected this paragraph.

Line435-437: ”. . .TEP concentrations had not reached the usually higher summer value yet since phosphate remained present in the water column (potentially not limiting the PP)”. Please make the relationship more clear.

AR: We modified this paragraph to make clear that even though we sample in June, the high Chla concentration and the phosphate still present in the water column could indicate that PP was not nutrient limited yet. The presence of nutrients (phosphate) may be an explanation of why TEP concentration was lower than reported before for summer in the Baltic Sea when PP was low due to nutrient limitation.

Line 444: It should be noted at what depth the OMZ was located before the salt water inflow. Recommendation for rewriting the sentence: The MBI changed the vertical distribution of O2 in the

GB by increasing its concentrations in depth below...m and relocation of the oxygen deficient layers from ..m to 74-140 m depth.

AR: We modified the text according to the reviewer recommendations

Line 452-453: “MBIs can have a major impact on nutrient recycling“. Such general statements should be reduced throughout the ms.

AR: This sentence was moved to the beginning of the paragraph since was introducing the effect of MBI in nutrient distribution.

Line 480: ”. . .. Carbon flux below the euphotic zone. . .”. To the bottom or to what depth?

AR: For clarification, this sentence was modified to “Our measurement of carbon flux at 40 m , below the euphotic zone, were…”

Line 485-486: “. . ..the estimations based on our results from the GB are higher than the C fluxes predicted by those models.” Here it should be taken into account that the measurements are obtained only from a single measurement over one or two days. The question is how representative a single measurement is. The subsequent paragraphs and chapter should be focused. At the moment it is very diffuse and the message is not clear.

AR: We agreed with the reviewer that our study represent only one discrete measurement; however, the objective of mention the results of previous estimations from modeling studies was precisely to add some context to our results.

We re-organize the discussion to make it clearer and more focus.

Table 3: It is not clear for me how the filamentous cyanobacteria were counted. Were the single cells in the filaments counted or were it counted as units of 50µm or 100µm length, as it is usually performed.

AR: The filamentous cyanobacteria were counted as single filament as it is usually performed. The word unicellular was deleted from the table.

Fig.2A: The scale of the x-Axis for salinity is wrong.

AR: We thank the reviewer for this observation; the salinity scale in figure 2a is fixed

In Fig. 4: It seems that only one or two depth are sampled. It should be indicated by zero-values if all depth are investigated and no particle is found.

AR: We added all values to figure 4, included the depths with zero particles.

Recommendation: Moderate revision Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-360, 201

Referee #2

Interactive comment on "Composition and Vertical Flux of Particulate Organic Matter to the Oxygen Minimum Zone of the Central Baltic Sea: Impact of a sporadic North Sea inflow"

by Carolina Cisternas-Novoa

T. Jilbert (Referee) tom.jilbert@helsinki.fi Received and published: 15 October 2018

In this study the authors use a wide range of analyses to investigate the vertical structure of suspended and sinking particulate matter composition in two stratified basins of the Baltic Sea following the MBI of 2014-2015. The data set is large and interesting, but I concur with the first reviewer's assessment that the study lacks a clear focal message. For this reason I would encourage the authors to streamline the text when making their revisions.

My principal scientific comment about the paper would be that the authors have not acknowledged the possibility that vertical profiles of dissolved and particulate constituents in the Gotland Basin may be influenced by displacement effects. Following the MBI of 2014-2015, the sub-halocline water column of the GB experienced significant turbulent mixing between 'old' and 'new' water masses. A lot of the changes in water chemistry that occurred during 2015 were caused by displacement of old, stagnant water by water masses associated with the MBI (see e.g. Myllykangas et al., ESD 8, 2017). For example, the low concentrations of Si(OH)4 and PO4 in the deepest samples of the GB (Fig. 2A) are very likely due to enhanced contribution of oxic, low-nutrient water at this depth, and not due to scavenging of these constituents onto MnOx particles as suggested by the authors for phosphate (Line 464 and in the Conclusions). Displacement may have also influenced the vertical structure of suspended and sinking particulate matter, so this angle should be included when interpreting the results. In addition I would urge the authors to check their text thoroughly for typographic, spelling and grammatical errors. I have highlighted a few in my minor comments but there are likely several more.

AR: We agreed with the reviewer that the displacement effects associated with the 2104/2015 MBI might have influenced the vertical profiles of dissolved and particulate constituent. Therefore, we add this aspect to the discussion (L478-484) of the vertical profile of nutrients (L504-510), vertical profile of particulate organic in the water column, and particulate organic matter fluxes (L554-558).

However, even when we acknowledge that the net effect of the MBI in the particulate organic matter (POM) distribution and export efficiency is a combination of physical effects and biogeochemical changes; this does not modify our conclusion. Our results suggest that changes in the water chemistry related to the MBI and the consequent transport or in-situ formation of MnOx due to the favorable redox conditions may impact the distribution, degradation, and of export of POM in the GB

Kind regards, Tom Jilbert

Minor comments

Line 61: spelling: "allochthonous"

AR: We corrected the spelling mistake.

Line 95: spelling and grammar: the correct spelling is ”Fårö”; Use “In the LD” rather than “At the LD”

AR: We corrected the grammar mistake

Line 110: rephrase (difficult to understand)

AR: We rephrased the sentence.

Line 156: grammar: Use “consisted of” rather than “consisted in”

AR: We changed the preposition

Line 166: what is the meaning of “caped”?

AR: We changed the word “capped” for “covered”

Line 181: grammar: Use “in duplicate” rather than “in duplicated”

AR: It has been fixed

Line 220: rephrase (difficult to understand)

AR: We rephrased the sentence

Line 321: spelling “below”

AR: We fixed the spelling of “below” in the ms

Line 354: what is the meaning of “and similar to the water column”?

AR: For clarity, we modified this sentence to “similar to the water samples,”

Line 356: word missing: “MnOx like were...”

AR: We fixed the sentence

Line 357: Remove colon (:) before “TEP”

AR: We removed the colon

Line 358: Define ESD

AR: We added the definition of equivalent spherical diameter (ESD) to the text.

Line 362: Avoid staring a sentence with an acronym

AR: This has been fixed

Line 375: add space before bracket. Also “Redfield’s” should be “Redfield ratio”

AR: We fixed those mistakes

Line 390: DI should be introduced and defined in the Methods section

AR: We added the definition and calculation of the DI to the method section.

Line 432: grammar: “may be enhanced”

AR: We changed this line

Line 437: typographic errors

AR: We fixed the typographic error

Line 444: typographic errors

AR: We fixed the typographic error

Line 451: “compounds” plural

AR: We corrected the word to “compounds”

Line 453: spelling: “phosphorus”

AR: We corrected the spelling of “phosphorus” in the ms.

Line 464: Rephrase and check grammar, tenses, etc.

AR: We rephrase and corrected the grammar of this paragraph.

Line 468-470: these statements belong in Results rather than Discussion

AR: We moved the statement to the results section

Line 489-90: typographic errors

AR: We modified this paragraph and fixed the errors.

Line 519: Mn2+ is not an electron acceptor

AR: We fixed this mistake

Line 526: PN and CSP are not compounds. Rephrase.

AR: We changed “compounds” to “components of POM”

Line 597: Nisken bottle, not CTD

AR: We replaced CTD by Niskin bottle

Table 2: should the units be “cells/mL)”?

AR: We modified how we showed the units to (cell ml^{-1})

Fig. 4: are these all the sampling depths for MnOX-like particles? If samples from other depths were studied but yielded zero particles, these should also be included in the plot

AR: We added all values to figure 4, included the depths with low number or zero particles.

Composition and Vertical Flux of Particulate Organic Matter to the Oxygen Minimum Zone of the Central Baltic Sea: Impact of a sporadic North Sea inflow

Carolina Cisternas-Novoa*, Frédéric A.C. Le Moigne, Anja Engel.

GEOMAR, Helmholtz Centre for Ocean Research Kiel, Düsternbrooker Weg 20, D-24105 Kiel

**Corresponding author:* Carolina Cisternas-Novoa, GEOMAR, Helmholtz Centre for Ocean Research Kiel, Düsternbrooker Weg 20, D-24105 Kiel, Germany, +49 431 600-4146 ccisternas@geomar.de

Keywords: Baltic Sea, Oxygen minimum zone, POC, PN, POP, TEP, CSP, Sediment trap, Export efficiency.

Abstract

Sinking particles are the main form to transport photosynthetically fixed carbon from the euphotic zone to the ocean interior via the biological carbon pump (BCP). Oxygen (O_2) depletion may improve the efficiency of the BCP. However, how the lack of O_2 mechanistically enhances particulate organic matter (POM) fluxes is not well understood. Here, we investigate distributions and fluxes of POM in two deep basins in the Baltic Sea (GB: Gotland basin and LD: Landsort Deep) with contrasting oxygenation regimes, resulting from a major oxygen-rich saltwater inflow event that oxygenated the bottom waters of GB but not the LD. In June 2015, we deployed surface tethered sediment traps in oxygenated surface waters (GB:40 and 60 m; LD: 40 and 55m), within the oxygen minimum zone (OMZ, GB: 110 m and LD: 110 and 180 m), and at deeper waters oxygenated by the inflow in GB (180 m). We hypothesize that the different O_2 conditions in the water column of the GB compared with the LD affected the POM distribution and caused differences in export efficiency between those two stations.

Fluxes and composition of sinking particles were different in the GB and the LD. In the GB, POC flux was 18% lower in the shallowest trap (40 m) than in the deepest sediment trap (at 180 m). Particulate nitrogen (PN) and Coomassie stainable particles (CSP) fluxes decreased with depth, and particulate organic phosphorus (POP), biogenic silicate (BSi), Chl *a*, and transparent exopolymeric particles (TEP) clearly peaked within the core of the oxygen minimum zone (OMZ, 110 m); this coincided with a high flux of manganese oxide (MnOx)-like particles. In the LD, POC, PN, and CSP fluxes decreased 28, 42 and 56% respectively from the surface to deep waters. POP, BSi and TEP fluxes, however, did not decrease with depth and were slightly higher in the 110 m sample. During this study, MnOx-like particle flux was two orders of magnitude higher in the GB (affected by the 2014/2015 North Sea inflow) relative to the LD.

Our results suggest that MnOx-like particles, formed after the inflow of oxygenated water into the GB, may form aggregates containing, not only transparent exopolymeric particles, as indicated previously, but also POC, POP, BSi, and Chl *a*. Aggregates composed of MnOx-like particles and POM may accumulate in the redoxcline, where they formed larger particles that eventually sink to

the seafloor. We propose that this mechanism would alter the vertical distribution and the flux of POM, and it may contribute to the higher transfer efficiency of POC in the GB. This idea is consistent with the fact that the OM reaching the seafloor was fresher and less degraded in the GB than in the LD.

1. Introduction

Sinking particles are the primary vehicles for transporting photosynthetically fixed carbon from the surface to the deep ocean via the BCP (Boyd and Trull, 2007; Turner, 2015). It has been suggested that the transfer of particulate organic carbon (POC) from the euphotic zone to the ocean interior is enhanced in oxygen minimum zones (OMZs) (Cavan et al., 2017; Devol and Hartnett, 2001; Engel et al., 2017; Keil et al., 2016; van Mooy et al., 2002). Possible mechanisms explaining the higher POC transfer include: i) the reduction of aggregate fragmentation due to the lower zooplankton abundance within the OMZ (Cavan et al., 2017; Keil et al., 2016); ii) a higher refractory nature of sinking particles (Keil et al., 2016; van Mooy et al., 2002); iii) a decrease in heterotrophic microbial activity due to oxygen limitation (Devol and Hartnett, 2001); iv) the preferential degradation of nitrogen-rich organic compounds (Kalvelage et al. 2013; Van Mooy et al. 2002, Engel et al. 2017), and v) changes in ballast materials that may alter the sinking velocity and protect organic matter from degradation (Armstrong et al., 2002). However, mechanisms of how low O_2 concentration would affect the composition and fate of sinking OM, and the efficiency of the biologic carbon pump in oxygen-deficient basins have hardly been investigated.

The semi-enclosed, brackish Baltic Sea is a unique environment with strong natural gradients of salinity and temperature (Kullenberg and Jacobsen, 1981), primary productivity, nutrients (Andersen et al., 2017), and O_2 concentrations (Carstensen et al., 2014a). New production, defined as the fraction of the autotrophic production supported by allochthonous sources of nitrogen (Dugdale and Goering, 1967) is considered equivalent to the particulate OM export (Eppley and Peterson, 1979; Legendre and Gosselin, 1989) on appropriate timescales. In the Baltic Sea, new production varies seasonally (Thomas and Schneider, 1999); spring and summer are periods of elevated new production supported by the diatom-dominated spring bloom and by

diazotrophic cyanobacteria, respectively (Wasmund and Uhlig, 2003). Based on sediment trap data, collected at 140 m depth in the Gotland Basin, Struck et al. (2004) reported that the highest fluxes of POC occur in fall, followed by summer and spring. Using $\delta^{15}N$ they showed that during the summer, N_2 fixation by diazotrophic species was the primary source (~41%) of the exported nitrogen, and that the majority of the particulate OM sedimenting in the central Baltic Sea is of pelagic origin.

OM export from the euphotic zone to the seafloor has a dual significance in the deep basins of the Baltic Sea. On the one hand, it contributes to the long-term burial of POC, and consequently to the removal and long-term storage of CO_2 from surface waters (Emeis et al., 2000; Leipe et al., 2011); on the other hand, it connects the pelagic and the benthic systems contributing to the oxygen consumption and hence deoxygenation at depth. Environmental and anthropogenic changes may alter the magnitude and composition of OM transferred from the surface to the seafloor in the Baltic Sea (Tamelander et al. 2017). The reduction of nutrient inputs as targeted by the Baltic Marine Environment Protection Commission (HELCOM) can cause a decrease in OM downward flux and limit the oxygen depletion. However, to fully suppress hypoxia enhanced ventilation would be necessary the bottom waters of the Baltic Sea.

The Gotland Basin (GB), and the Landsort Deep (LD) are the deepest basins of the Baltic Sea. They exhibit permanent bottom-water hypoxia (Conley et al. 2002), caused by a combination of limited water exchange with the North Sea through the Kattegat Strait, strong vertical stratification, and high production /remineralization of OM due to eutrophication (Carstensen et al., 2014b; Conley et al., 2009). From the1950s to 1970s, the hypoxic zones (<60 µmol O_2 kg^{-1}) in the Baltic Sea had expanded fourfold (Carstensen et al. 2014). Salt-water inflows from the North Sea are the primary mechanism renewing deep water in the central Baltic Sea. A Major Baltic Inflow (MBI) occurred in 2014/2015 (Mohrholz et al. 2015); this event ventilated bottom waters for five months between February and July 2015 (Holtermann et al., 2017). The 2014/2015 MBI caused the intrusion of O_2 to deep hypoxic waters, a substantial temperature variability (Holtermann et al., 2017), the displacement of remnant stagnant water masses by new water that

changed the chemistry of the water column (Myllykangas et al., 2017), and high turbidities that may be associated with redox reactions products (Schmale et al., 2016). At the time of sampling (June 2015), this MBI had reached the Gotland Basin , but did not affect the LD, located further northwest. In the LD, water properties did not change due to the MBI, the sulfidic layer was maintained (hydrogen sulfide, H_2S concentrations of 20.7- 21.2 μM), and salinity varied between 10.6 and 10.9 (Holtermann et al., 2017).

In the GB and the LD, a permanent transition zone of about 2 to 10 m thickness separates the surface oxygenated and the oxygen-deficient waters; the approximated position of the pelagic redoxcline is between 127 and 129 m in the GB and between 79 and 85 m in the LD (Glockzin et al., 2014). The water column stratification ~~is zone known as "pelagic redoxcline"~~ is only disrupted by sporadic intrusions of saline, well-oxygenated waters from the North Sea (Günter et al., 2008). In the GB, the 2014/2015 MBI oxygenated the deep water column, removed the sulfidic waters in the deeper layers below the redoxcline, and created a secondary near-bottom redoxcline (Schmale et al., 2016). A steep redox gradient characterizes the pelagic redoxcline; here electron acceptors and their reduced counterparts are vertically segregated, and biogeochemical transformations mediated by microbial processes are actively occurring (Bonaglia et al., 2016; Brettar and Rheinheimer, 1991; Neretin et al., 2003). For instance, iron (Fe) and manganese (Mn) undergo rapidly reversible transformations at the redox interface. Under anoxic conditions, these metals are present in dissolved reduced forms Mn(II) and Fe(II); under oxic conditions or in presence of nitrate they react with O_2 and form particulate oxides. Manganese oxides (MnOx) production may be microbially mediated (Neretin et al., 2003; Richardson et al., 1988), or authigenic (Glockzin et al., 2014). The reduction of Mn(IV) with sulfide occurs within a scale of seconds to minutes (Neretin et al., 2003), and is inhibited by nitrate (Dollhopf et al., 2000). The sporadic oxygenation of the deep water of the GB combined with the release of Mn from the sediments into the water column (Lenz et al., 2015) generate appropriate conditions for particulate MnOx formation. MnOx particles have previously been observed in pelagic redoxclines in the Baltic Sea (Glockzin et al., 2014; Neretin et al., 2003). They are amorphous or

star-shaped particles that can occur as single particles or form aggregates enriched in OM (Neretin et al., 2003), specifically with transparent exopolymer particles (TEP) (Glockzin et al., 2014). TEP are highly sticky, polysaccharide-rich particles that can enhance aggregation and the formation of marine snow (Engel, 2000; Logan et al., 1995). Thus, MnOx-OM aggregates may significantly contribute to the downward flux of POC. However, TEP are less dense than seawater (Azetsu-Scott and Passow, 2004); therefore they could also reduce the density of marine aggregates and decrease their sinking velocity if the ratio of dense particles to TEP is too small (Azetsu-Scott and Passow, 2004; Engel and Schartau, 1999; Mari et al., 2017). Mixed aggregates containing MnOx and TEP have reported before for the GB and LD (Dellwig et al. 2010; Glockzin et al. 2014). Their sizes ranged between 0.8 and 41 μm equivalent spherical diameter (ESD), and their sinking velocity (0.76 m d^{-1}) was lower than what was predicted by the Stokes' law (Glockzin et al., 2014) possibly due to their star-shaped morphology and the high OM content attached to them. Additionally, MnOx aggregates may affect the cycling of particle-reactive elements like phosphorus and trace metals via scavenging processes (Dellwig et al., 2010). To date, there are no measurements of the density of MnOx-OM aggregates, their potential ballast effect of sinking OM, or their effect on the flux of particle-reactive elements in the Baltic Sea.

The objectives of this study are, first, to characterize the amount and composition of particles sinking out of the euphotic zone in two deep basins of the Baltic Sea: the GB and the LD. Second, to study how the oxygenation of deep waters (below 140 m) in the GB caused by the 2014/2015 MBI will affect the sinking fluxes of POM compared with LD that was not affected by the MBI and exhibited low O_2 concentration (below 74 m) and sulfidic conditions (below 160 m) in the deep water. We hypothesize that the MBI that altered the water column chemistry and created different O_2 conditions in the GB compared with the LD affected the abundance and *in-situ* formation of MnOx rich-aggregates and subsequently OM distribution causing differences in degradation and export of OM between those two stations.

2. Methods

2.1. Sampling location and water column properties

Samples were collected during the BalticOM cruise in the Baltic Sea onboard the *RV Alkor* form June 3th to June 19th, 2015. We collected sinking particles using surface-tethered sediment traps (Engel et al., 2017; Knauer et al., 1979) in the GB and the LD (Fig.1). Additionally, water column samples (table 2) were collected using a Niskin-bottle rosette at the locations of the trap deployments. Temperature, salinity and O_2 concentration were determined at each station using a Sea-Bird (CTD) probe equipped with a oxygen (Oxyguard, PreSens), calibrated with discrete samples measured using the Winkler method (Strickland and Parsons, 1968; Wilhelm, 1888).

2.2. Sediment trap design and deployment

We deployed two surface-tethered sediment traps for two days in the GB, and one day in the LD (Fig.1). Each trap collected particles at four depths 40, 60 (55 in LD), 110 and 180 m (Table 1) to estimate POM fluxes to and within the OMZ. The sediment trap consisted of five (two traps were located at 40 m in each station to evaluate replicability) arrays of 12 acrylic particle interceptor tubes (PITs) mounted in a PVC cross frame; each tube was equipped with an acrylic baffle at the top to minimize the collection of swimmers (Engel et al., 2017; Knauer et al., 1979). The PITs were 7 cm in diameter and 53 cm in height with an aspect ratio of 7.5 and a collection area of 0.0038 m^{-2}. The cross frame and PITs were attached to a line that had a bottom weight and a set of surface and subsurface floats. The procedures for PIT preparation and sample recovery followed Engel et al. (2017). Shortly before deployment, each PIT was filled with 1.5 L of seawater previously filtered through a 0.2 μm pore size cartridge. A preservative solution of saline brine (50 g L^{-1}) was added slowly to each PIT underneath the 1.5 L of filtered seawater, carefully keeping the density gradient. The PITs were kept covered until deployment and immediately after recovery to avoid contamination. After recovery, the density gradient was visually verified, and the supernatant seawater was siphoned off the PIT. Then, the remaining bottom waters (approx. 0.6 L) containing the particles were pooled together and filled-up to 10 L with filtered seawater. After that, the samples were screened with a 500 μm mesh to remove swimmers. Subsequently, samples were split into aliquots that were processed for the different biogeochemical analysis as described in Engel et al. (2017).

2.3. Biogeochemical analysis

Nutrients were measured in seawater samples of the deployment stations. Ammonium (detection limit 0.05 µM) was measured directly on unfiltered seawater samples on board after Solórzano (1969). Phosphate, nitrate, and nitrite (detection limit 0.04 µM) were filtered through a 0.2 µm pore size and stored frozen until their analysis; samples were measured photometrically with continuous flow analysis on an auto-analyzer (QuAAtro; Seal Analytical) after Grasshoff et al. (1999).

Particulate organic carbon (POC), nitrogen (PN), organic phosphorus (POP), and chlorophyll a (Chl *a*) were determined as described in Engel et al. (2017). Aliquots of 100 to 200 ml of the trapped material, and 500 ml for the sampled seawater were filtered in duplicate for each parameter at low vacuum (<200 mbar), onto pre-combusted GF/F filters (8h at 500°C). T~~After filtration, t~~he filters were stored frozen (-20°C) until analysis. Prior analysis, filters for POC-PN determination were exposed to acid fumes (37% hydrochloric acid) to remove carbonates, and subsequently dried for 12h at 60 °C. POC and PN concentrations were determined using an elemental analyzer (Euro EA, Hechatech) after Sharp (1974).

POP was analyzed after Hansen and Koroleff (1999). POP was oxidized to orthophosphate by heating the filters in 40 mL of deionized water (18.2MΩ) with Oxisolv (MERCK 112936) for 30 min in a pressure cooker. Orthophosphate was determined spectrophotometrically at 882 nm in a Shimadzu UV-VIS Spectrophotometer UV1201.

Chl *a* was analyzed after extraction with 10 mL of 90% acetone, the fluorescence of the samples was measured using a Turner fluorimeter (440/685 nm, Turner, 10-AU) according to Strickland et al. (1972). The fluorometer was calibrated with a standard solution of Chl *a* (Sigma-Aldrich C-5753).

Phytoplankton composition and abundance in the stations where we deployed sediment traps were evaluated using light microscopy and flow cytometry. Phytoplankton, > 5 µm, was counted and identified in 50 ml of fixed samples (Lugol's solution, 1% final concentration) using a Zeiss Axiovert inverted microscope (200x magnification). The size of the counted phytoplankton

species ranged from 10 to 200 µm. Phytoplankton, <20 µm, cell abundance was quantified using a flow cytometer (FACSCalibur, Becton, Dickson, Oxford, UK). 2 ml samples were fixed with formaldehyde (1% final concentration) and stored frozen (-80 °C) until analysis (two weeks later). Cell counts were determined with CellQuest software (Becton Dickenson); pico- and nanoplankton populations of naturally containing chlorophyll or phycoerythrin (*i.e.*, Synechococcus) were identified and enumerated.

Biogenic silica (BSi) was determined by filtering duplicate aliquots of 50 to 100 mL onto 0.4 µm cellulose acetate filters. Samples were stored at -20°C until analysis. For the measurements, filters were digested in NaOH at 85°C for 135 min; the pH was adjusted to 8 with HCl. Silicate was measured spectrophotometrically according to Hansen and Koroleff (2007).

Transparent exopolymeric particles (TEP) and coomassie stainable particles (CSP) from trap and water column were analyzed by microscopy according to Alldredge et al. (1993) and Long and Azam (1996) respectively. Duplicate aliquots of 5 to 20 ml were filtered onto 0.4 µm Nuclepore membrane filters (Whatmann) and stained with 1 ml of Alcian Blue solution for TEP and Coomassie brilliant blue solution for CSP. Filters were transferred onto Cytoclear ® slides and frozen (-20°C) until microscopy analysis. For the analysis, thirty images for each filter were captured under 200x magnification using a light microscope (Zeiss Axio Scope A.1) connected to a color camera (AxioCam MRc). Particle abundance and area were measured semi-automatically using an image analysis system including the WCIF ImageJ software. The RGB was split in three channels: red, blue and green, and the red was used to quantify the amount of TEP and CSP (Engel 2009). Additionally, TEP and CSP in water samples from the stations where we deployed sediment traps were analyzed spectrophotometrically (with higher vertical resolution than microscopy) according to Passow and Alldredge (1995) and Cisternas-Novoa et al. (2014) respectively. Concentrations of TEP are reported relative to a xanthan gum standard and expressed in micrograms of xanthan gum equivalents per liter (µg XG eq. L^{-1}), and concentrations of CSP are reported relative to a bovine serum albumin standard and expressed in micrograms of bovine serum albumin equivalents per liter (µg BSA eq L^{-1}).

The abundance of MnOx-like particle was determined by image analysis, using the same images that for TEP and CSP analysis and a modified version of the method described above. Thirty images per filter (200x) were analyzed semi-automatically using Image J. The blue channel was used to quantify the amount of MnOx-like particles in the water column and sediment traps, in this manner, the MnOx-like particles were clearly visible with a negligible disruption from TEP or CSP stained blue.

Total amino acids (TAA) were analyzed in unfiltered seawater and trapped material. Samples were stored at -20°C until analysis. Duplicate samples were hydrolyzed at 100 °C in 6N HCl (Suprapur® Hydrochloric acid 30%) and 11 mM ascorbic acid for 20h. Amino acids were separated and measured by high-performance liquid chromatography (HPLC), after derivatization with ortho-phthaldialdehyde using a fluorescence detector (Excitation/Emission 330/445 nm) (Dittmar et al., 2009; Lindroth and Mopper, 1979). The quantitative degradation index (DI) of Dauwe et al. (1999), based on changes in amino acids composition of the POM as it undergoes to degradation processes in the water column, was calculated using the factor coefficient of Dauwe et al. (1999) and the average and standard deviation of the TAA of this data set.

Total combined carbohydrates (TCHO) were determined by ion chromatography according to Engel and Händel (2011). TCHO were analyzed in the unfiltered seawater and sediment trap material. Samples were stored at -20°C until analysis. Prior to analysis, the samples were desalted by membrane dialysis using dialysis tubes with 1 kDa molecular weight cut-off (Spectra Por). The desalination was conducted for 4.5 h at 1°C. Then, a 2 mL subsample was sealed with 1.6 mL 1M HCl in pre-combusted glass ampoules and hydrolyzed. Samples were hydrolyzed for 20 h at 100°C. After hydrolysis, the subsamples were neutralized by acid evaporation under N_2 atmosphere at 50°C, resuspended with ultrapure Milli-Q water and analyzed by ion chromatography.

2.4 Statistics

Significant differences between two parameters were tested using the Mann-Whitney U-test. The results of statistical analyses were assumed to be significant at *p*-values < 0.05. Statistical analyses were performed using Matlab software (MatlabR2014a).

3. Results

3.1. Biogeochemistry of the water column

The water column of both stations was stratified during the study. In the GB the seasonal thermocline was located between 22 and 37 m, the temperature decreased rapidly from 9.8°C in the surface mix layer to 4.7°C below 37 m. Deeper in the water column, a pycnocline (halocline) coincided with the oxycline and was located between 65 m (S=7.6) and 80 m (S=10.2), below 80 m the salinity gradually increased up to 13.5 at the bottom (220 m). In the GB, a hypoxic layer (<40 μmol O_2 L^{-1}) was located between 74 and 140 m; the core of the OMZ (<10 μmol O_2 L^{-1}) was located between 96 and 125 m. The O_2 concentration increases from 35 μmol O_2 L^{-1} at 140 m to 79 μmol O_2 L^{-1} at 220 m (Fig. 2a). In the LD, the seasonal thermocline was located between 10 and 39 m, where the temperature decreased gradually from 12°C to 4.0°C (Fig. 2b). The pycnocline was between 55 (S=7.2) and 75 m (S=9) below that the salinity is constant (S=10.7) until the bottom of the station (430 m). The O_2 concentration was below the detection limit (<3 μmol O_2 L^{-1}) from 74 m to the bottom.

The vertical profile of nutrients was different at both stations (Fig. 2). In the GB, nitrate concentration increased from below the detection limit, in the upper ten meters, to 0.17 μM at 40 m (Fig. 2a). Concentrations were variable within the OMZ with 6 μM in the upper (80 m) and lower oxycline (140 m), and 0.12 μM in the core of OMZ (110 m); the nitrate concentration decreased to 4.8 μM in the deepest sample (220 m). Nitrite was below the detection limit in most of the water column except for 60 m (0.09 μM) and 110 m (0.11 μM). Ammonium increased from 0.14 μM in upper ten meters to 1.15 μM at 40 m; concentrations were variable in the OMZ with less than 0.15 μM in the upper (80 m)

and lower oxycline (140 m), and maximum concentration of 3.28 ± 0.01 μM in the core of the OMZ (110m). Vertical profiles of phosphate and silicate at the GB were similar; the concentrations steadily increased from the upper ten meters of the water column (0.29 μM and 10.36 μM respectively) to the OMZ (2.67 μM and 39.07 μM respectively), and gradually decreased below the OMZ (Fig. 2a). Hydrogen sulfide was not detectable in the GB.

In the LD, nitrate and nitrite concentrations were below the detection limit between the surface and 250 m (<0.04 μM) (Fig. 2b). Nitrite showed a maximum of 0.22 μM at 350 m, and nitrate a maximum of 6.0 μM at 400 m. Ammonium concentrations varied between 0.06 and 0.59 μM in the upper 70 m and increased to 5.97 and 8.03 μM in the OMZ (below 74 m). The lowest concentration (0.07μM) was measured in the surface and maximum concentration of 8.03 μM at 110 m. Phosphate and silicate concentrations were relatively low within the mixed layer due to phytoplankton consumption; gradually increased below the pycnocline, and decreased between 110 and 180 m. Phosphate concentrations varied between 1.5 and 2.5 μM in the upper 110 m of the water column, decreased to 0.22 μM at 180 m and increased to 2.7 μM at 430 m (deepest sample). Silicate ranged between 25 and 38 μM in the upper 110 m of the water column, decreased to 7.4 μM at 180 m, and increased 38.9 μM at 430 m ~~of the water column~~. Hydrogen sulfide was detectable below 180 m, with the highest concentration (3.97 μM) at 250 m and the lowest (0.04 μM) between 300 and 350 m (Fig. 2b).

3.2. Particulate organic matter concentration in the water column

Chl *a* concentration in the upper 10 m was slightly higher in the GB (1.5-1.7 μg L^{-1}, Fig. 3b) than in LD (1.4-1.2 μg L^{-1} and 0.1-0.3 μM, Fig. 3e). In both stations, more than 90% of the total smaller phytoplankton (<20 μm, pico- and nanophytoplankton) abundances, determined by flow cytometry, were measured in the upper 60 m, although phytoplankton was detectable in the entire water column. Pico- and nanophytoplankton abundances were 10% higher in GB than in LD (Table 2). Picocyanobacteria determined by phycoerythrin fluorescence account for 92% and 96%

of the total picophytoplankton in GB and LD respectively. Picocyanobacteria was 30% higher in GB than in LD.

Large phytoplankton (>5 μm) abundance, determined by microscopy, was 63% higher in the LD than in the GB (Table 3). Filamentous cyanobacteria dominated the large phytoplankton community at both stations with up to 90% corresponding to *Aphanizomenon* sp. Cyanobacteria represented 56% of the total phytoplankton counts in the GB and up to 74% in the LD. Dinoflagellates (dominated by *Dinophysis* sp.) were significant in both stations (19% of the total), whereas chlorophytes (dominated by filaments of *Planctonema* sp. containing cylindrical cells) were more abundant in the GB than in LD (25% and 4% of the total phytoplankton respectively). Diatoms represented less than 1% of the phytoplankton in both stations, and they were slightly more abundant at 40 m in the LD (Table 3). BSi was higher in the upper 10 m (0.4-0.5 μM) and decreased with depth in the GB (Fig. 3b), whereas in the LD, BSi showed a peak at 40 m and then decreased with depth (Fig. 3f).

Vertical profiles of POC, PN, and POP concentration were similar in the water column of the two stations (Fig. 3a, d). In the GB, the concentrations were higher in the upper 10 m of the water column (POC: 40.38 ± 0.80, PN: 3.89± 0.01, and POP: 0.26± 0.04 μM) and decreased gradually with depth until 110 m where relatively high concentrations (POC 18 ± 0.63, PN: 2± 0.08, and POP: 0.2 μM) were observed. The lowest concentrations were found at 180 m (POC: 11.97 ± 1.03, PN: 1.05± 0.02, and POP <0.03 μM) (Fig. 3a). In the LD, POM decreased with depth from the surface (POC: 35 ± 0.99, PN: 4± 0.09, and POP: 0.2 μM) to 40 m, remained relatively constant between 40 and 80 m and decreased again between 110 and 250 m (Fig. 3d).

We observed high concentrations of TEP and CSP in the upper 10 m in both stations. The highest TEP concentration was measured at 1 and 10 m at both stations, and it was slightly higher (19%) in the GB than in the LD (Fig. 3c, f). TEP and CSP vertical profiles were different from each other in the GB (Fig. 3c) and covaried in the LD (Fig. 3f). Like observed for POC, PN, and POP, TEP concentrations showed a peak at 110 m (50.29± 6.17 μg XG eq. L^{-1}) in the GB. The highest concentration of CSP at this station was observed in the shallowest (1 m) sample, CSP

concentration decreased quickly below 10 m, and then it increased at 140 and 230 m (the deepest sample ~20 m above the seafloor) (Fig. 3c). In the LD, the highest concentrations of TEP and CSP were measured in surface (1 and 10 m) and at 110 m (Fig. 3f). TEP and CSP decreased with depth in the first 80 m (from 53.26± 7.10 to 18.39± 4.57 μg XG eq. L^{-1} and from 53.26± 7.10 to 31.57± 18.78 μg BSA eq. L^{-1}). Both types of gel-like particles showed an increase in concentration at 110 m (49.25± 4.08 μg XG eq. L^{-1} and 66.89± 22.33 μg BSA eq. L^{-1} respectively). Below 110 m, TEP concentrations stayed relatively constant, while CSP concentrations decreased at 180 m and kept relatively constant below that depth.

3.3. MnOx-like particles vertical distribution in the water column

Dark, star-shaped, MnOx-like particles (Glockzin et al., 2014; Neretin et al., 2003) were only observed below the fully oxygenated mixed layer in the GB and, in less abundance, in the LD (Fig. 4). In GB, single MnOx-like particle and large aggregates were observed from 80 m to 220 m (the deepest sample, approximately 28 m above the seafloor). Relatively high concentration of MnOx-like particles ($2x10^6$ particles L^{-1}), were measured in the upper (80 m) and lower (140 m) oxycline where the O_2 concentration was less than 40 μM, and at 220 m ($4x10^6$ particles L^{-1})(Fig. 4a). The lowest abundance of MnOx-like particles ($7x10^5$ particles L^{-1}) was observed at 110 m, in the core of the OMZ where the O_2 concentration was less than10 μM. The equivalent spherical diameter (ESD) varied between 0.6 and 30.5 μm and the median was 3.0 μm. The largest aggregates were observed in the upper oxycline (80 m). In the LD, MnOx-like particles were less abundant, smaller and had a narrow distribution in the water column than in the GB. MnOx-like particles were not detected in the fully oxic (0-40 m) or fully anoxic (180 to 430 m) water column. At 60 m, right above the oxycline, MnOx-like particles began to appear, however, in relatively low abundance. The maximum abundance, $9x10^5$ particles L^{-1}, was observed in the oxycline at 70 m (Fig. 4b). The ESD varied ranged between 0.6 and 13.4 μm, the largest aggregates were observed at 70 m.

3.4. Fluxes of Particulate Organic Matter

Fluxes of POC and PN varied little with depth in the GB (Fig. 5a-b). POC flux slightly increased (18%) from the shallowest (40 m) to the deepest (180 m) sediment trap. Fluxes of PN and CSP were higher at 40 and 60 m and decreased (19 and 70 %) from 60 to 180 m, respectively (Fig. 5a and 5c). On the other hand, fluxes of POP, BSi, Chl *a* (Fig. 5b) and TEP (Fig. 6a) peaked in the sediment trap located in the core of the OMZ (~110 m). The increment of fluxes at 110 m coincided with the presence of abundant MnOx-like particles associated with TEP (Fig. 6a). In addition, TEP size distribution, determined by image analysis, indicated an increase in large TEP at 110 m (data not shown). In contrast, in the LD, POC, PN (Fig. 5d) and CSP (Fig. 6d) fluxes, steadily decreased with depth by 28, 42 and 56% from 40 to 180 m. Similar to the fluxes measured in the GB, the POP, BSi (Fig. 5e) and TEP (Fig. 6c) showed a smaller peak in the sediment trap located at 110 m.

MnOx-like particles were drastically less abundant in sediment trap samples from the LD than in the GB and when present, they appear as single particles, not aggregated with TEP or CSP (Fig. 6c, d). At both stations, and similar to the water column samples, MnOx-like particles were not observed in sediment trap samples collected, in fully oxygenated depths (40 and 60 m). The flux of MnOx-like particles at 110 and 180 m was two orders of magnitude larger in the GB than in the LD (Table 4). In the GB, MnOx-like particles were present in the sediment traps at 110 m and 180 m. They occurred as single particles and forming aggregates with each other and other particles such as TEP (Figure 6a, ~~-~~e), phytoplankton cells, or detrital material. The ESD of MnOx-like particles and aggregates ranged from 0.6 to 167 μm (median 2.8 μm) at 110 m and from 0.6 to 153 μm (median 3.3 μm) at 180 m. In the LD, only a few, single MnOx-like particles were observed at 110, their size ranged from 0.6 to 16.5 mm (median 1.8) (Table 4).

Total hydrolyzable amino acids (TAA) flux ranged from 371±12 to 501± 33 μmol $m^{-2}d^{-1}$ in the GB and from 502± 84 to 785± 54 μmol $m^{-2}d^{-1}$ in the LD (Fig. 7a). In the GB, the flux decreased with depth whereas, in the LD, the TAA flux at 40 m was lower than at 60 m and decreased with depth from 60 to 180 m (Fig. 7b). Vertical profile of TCHO flux was similar in both stations. The TCHO flux varied between 303± 8 and 428± 14 μmol $m^{-2}d^{-1}$ in the GB (Fig. 7a) and between

503± 19 and 584± 8 μmol $m^{-2}d^{-1}$ in the LD (Fig. 7b). In both stations, TCHO flux increased from 40 to 110 m, where the highest TCHO flux was measured, and then TCHO flux decreased at 180 m. The TCHO flux at 180 m was 22% higher than at 40 m in the GB, and the same that at 40 m in the LD.

3.5. *Chemical composition of sinking and suspended OM*

The molar ratios of suspended and sinking OM may be compared to the classical Redfield ratio for living plankton (106C: 16N: P; Redfield et al., 1963). Sinking OM was slightly above Redfield ratios at both stations. The POC:PN ratio of the sinking OM in both GB and LD were not significantly different. In the GB, the POC:PN ratio of the sinking OM increased with depth from 9.8 to 12.6. Contrastingly, in the suspended OM, POC:PN ratios were higher in the GB compared to the LD ($p<0.001$; Mann–Whitney U-test). In the GB, the POC:PN ratio of suspended OM varied between 8.4 and 12 without a clear trend with depth; while in the LD, decreased with depth from 8.7 (at 1m) to 6.2 (at 400m), and a slightly higher value of 7.8 was observed at 430 m. In the LD the POC:PN of sinking OM was significantly lower than in suspended OM ($p<0.001$). The POC:POP molar ratio of sinking OM was lower ($p<0.05$) in the GB than in the LD; and it was higher ($p<0.01$) in sinking than in suspended OM in the LD (Table 5). The POC:BSi molar ratio was lower in sinking than in suspended OM in both stations (GB: $p<0.05$; LD: $p<0.01$). In sinking OM, the POC:BSi ratio was below Redfield value, whereas in suspended OM it was above Redfield ratio (Table 5). The PN:POP molar ratio was lower in sinking OM than in suspended OM in both stations ($p<0.001$). In sinking OM this value was always below the Redfield ratio, while in suspended OM, it was always above the Redfield ratio.

At both stations, the fraction of sinking POC composed of AA was larger than in suspended OM. Similarly, the C contained in CHO made up a larger percentage in sinking OM than in suspended OM (Table 5). The amino acid-based degradation index (DI, Dauwe et al., 1999) in sinking OM varied from 0.1 to 1.14 and was higher than in suspended OM (-1.25 to -0.42). The DI was higher in the GB than in the LD in sinking and suspended OM. In the sinking OM of the GB, the DI decreased with depth but in the LD was more positive at 110m than at 60 m (Table 5).

4. Discussion

In this study, we described the results of 1) the characterization of the surface biogeochemical conditions and the sinking particles produced in the euphotic zone of the GB and the LD, during early summer 2015, 2) the flux, and vertical profile of sinking and suspended particles in the two basins. Our results suggested that the intrusion of oxygenated water to the GB associated with the 2014/2015 MBI caused changes in the water chemistry that affected the chemical composition and degradation stage of the sinking and suspended OM. This resulted in differences in the composition and magnitude of the sinking particle flux between GB and LD.

4.1 Characterization of biogeochemical conditions in GB and LD

Temperature, O_2, and inorganic nutrient concentrations were similar in euphotic zone (upper 20 m) at both stations. Moreover, though there were slight differences in biogeochemical conditions, such as phytoplankton biomass, phytoplankton composition and concentration and chemical composition of POM, in the surface water column, those were not significant. The concentration of Chl *a* (Fig. 3) and the abundance of picophytoplankton and nanophytoplankton (Table 2) were slightly higher (20 and 10 % respectively) in the GB than in the LD. This agrees with estimates of integrated total primary production, which were 10% larger in the GB (380 mg C m^{-2} d^{-1}) than in the LD (334 mg C m^{-2} d^{-1}; Piontek et al., unpublished). At both stations, picophytoplankton dominated the small phytoplankton (Table 2). These findings coincide with what was described previously for early summer~~,~~ in the Baltic Sea that indicate that during this period the productivity is sustained mostly by nano- and picophytoplankton communities (Leppänen et al., 1995) which co-existed with cyanobacteria and other phytoplankton species (Kreus et al. 2015). Microscopic analysis of larger phytoplankton (>5 µm), on the other hand, showed that filamentous cyanobacteria *Aphanizomenon* sp. (up to 200 µm large) was the dominant type on this size fraction in the upper 40 m (Table 3). *Aphanizomenon* sp. and *Nodularia spumigena*, are known to form summer blooms in the Baltic Sea, where they accumulate at the sea surface of the thermally stratified water column (Bianchi et al., 2000; Nausch et al., 2009; Wasmund, 1997). The medians of the cell abundance of total phytoplankton (>5 µm, table 3) in the upper 40 m of the water column were not significantly different (p=0.74) in the GB and the LD.

POC, PN, POP, BSi were slightly higher in the surface waters of the GB than in the LD; while , TEP and CSP concentrations in the surface waters were similar at both stations (Fig. 3). The concentration of TEP was higher than of CSP, both types of gel-like particles were most abundant in the euphotic zone indicating a phytoplankton origin. In the surface water column, TEP concentrations (48 and 62 μg X.G. Eq. L^{-1} in the GB and the LD, respectively) were 69 and 76% lower than the value previously reported for summer in the central Baltic Sea in June (200 μg X.G. Eq. L^{-1}) (Engel et al., 2002). Likewise, our dissolved inorganic nitrogen concentrations were below the detection limit in the surface; however phosphate concentrations were higher (0.2-0.65 μM) than the ones on the Engel et al. (2002) study. Mari and Burd (1998) reported that TEP concentration peaked during the spring bloom and in summer in the Kattegat. TEP production may be enhanced by enviromental conditions such as nutrient limitation (Mari et al., 2005; Passow, 2002), which are characteristic of late summer in the Baltic Sea (Mari and Burd 1998). Surface satellite-derived Chl-a concentrations in the Gotland Deep indicate that our samples were collected during Chl-a peak in mid-June (8–10 μg L^{-3}). Chl-*a* concentrations increased constantly from mid-May to the sampling period (Le Moigne et al., 2017), thus, likely TEP concentrations had not reached the usually higher summer value yet since the high concentration of Chl-a and presence of phosphate in the water column may suggest that the PP was not nutrient limited). Another possible explanation for the rather low concentrations of TEP could be that TEP may be removed from the surface by aggregation and subsequent sedimentation during the spring bloom due to the high abundance of cells and detrital particles during this time (Engel et al., 2002).

Although the composition and amount of OM in the surface waters at the two trap stations were similar, below the euphotic zone (40 m) the vertical profile of nutrients and POM concentrations were clearly different; likely due to the 2014/2015 MBI (Holtermann et al., 2017) that reached the deep waters of the GB. This inflow changed the salinity in the deepest waters and the vertical distribution of O_2 increasing its concentrations below140 m and constraining the oxygen-deficient layers from 74 m to 140 m depth. The water intrusion showed similar features as the new water masses and water pushed out of the Bornholm Basin (Schmale et al., 2016). The combination of

physical effects (the displacement of water masses, turbulent mixing and lateral transport) and the consequent development of redox conditions through 2015 may have impacted the distribution of MnOx and POM in the GB. In contrast, the LD maintained permanent suboxic (<5 μmol L^{-1}) waters below 74 m and hydrogen sulfide was detectable at 180 and 250 m (Fig. 2).

MBIs can have a major impact on nutrient recycling. In the GB nitrate concentration increased possibly as a consequence of the oxidation of reduced nitrogen compounds (e.g., ammonium, ammonia and organic nitrogen compounds like urea) (Le Moigne et al., 2017) that accumulated during the stagnation (anoxic) period previous to the MBI (Hannig et al., 2007). Phosphorus could bind to iron hydroxides and MnOx and settle down during oxic conditions, building up a phosphate pool in the sediments that later on when the O_2 decreases close to the sediments, it may become a source of phosphate (Gustafsson and Stigebrandt, 2007). In addition to changes in O_2 concentration, the MBI altered the redox conditions in the GB creating a secondary redoxcline at 140 m, where the O_2 and the MnOx-like particles concentration increased (Fig. 4a). One consequence of those changes is the vertical extension of the layer in which MnOx aggregates could form. A previous study showed that MnOx might precipitate from the water column of the GB following a MBI event (Lenz et al., 2015). Scavenging of phosphate into Mn or Fe oxides had been shown in previous studies (Neretin et al., 2003). Moreover, Gustafsson and Stigebrandt, 2007 showed that there is a downward flux of phosphate, associated with particulate iron and MnOx, from the oxygenated water column to the anoxic deep waters. On the other hand, the intrusion of oxygenated water masses associated with the MBI caused turbulent mixing the deep water of the GB. Myllykangas et al. (2017) reported that following the 2014/2015 MBI, the GB experienced the displacement of stagnant water masses by the new water masses intruded during the MBI. Thus, the low concentrations of silicate and phosphate that we measured in the deep waters of the GB may also be a direct consequence of the intrusion of oxygenated, low-nutrient waters associated with the MBI. In contrast, in the LD, the water column remained suboxic down the sea floor (430 m), below the oxycline an increase of ammonium was observed (Fig.2b) which

could be an indicator for anaerobic respiration of OM, e.g., denitrification (Bonaglia et al., 2016; Hietanen et al., 2012).

In summary, although the GB and the LD had similar surface conditions in terms of phytoplankton production and POM stocks, during this study, we found differences the vertical concentration of nutrients (Fig. 2) and POM (Fig. 3) in the GB, ventilated by the MBI, relative to the LD, a station that remains suboxic. Our results suggest that physical processes and differences in the vertical profile of O_2 may modify the redox conditions of the water column, enhance the formation of MnOx-like particles (Fig. 4) that may aggregate with POM in the GB (or transported to the GB by the inflow) influencing the vertical distribution of POM in the water column.

4.2 Potential influence of O_2 concentration and redox conditions on sinking fluxes of POM in the GB and the LD

During this study, we also investigated the effect of different O_2 concentrations and redox conditions on the fluxes of particles. Our measurement of carbon flux at 40 m, below the euphotic zone, were 11.7±0.82 mmol C m^{-2} d^{-1} in the GB and 19.8±1.22 mmol C m^{-2} d^{-1} in the LD. Extrapolating those measurements to annual flux we obtain 4.37±0.31 mol C m^{-2} a^{-1} in the GB and 7.44±0.46 mol C m^{-2} a^{-1} in the LD. Our results from the LD are ~~compable~~ in the same range that~~with~~ the long-term annual estimations from models that varied between 3.8 to 4.2 mol C m^{-2} d^{-1} (Kreus and Schartau, 2015; Sandberg et al., 2000; Stigebrandt, 1991) for the Baltic Sea; however, the estimations based on our results from the GB are higher than the C fluxes predicted by those models.

The vertical flux of POM was different in the two studied stations. In the GB, the POM fluxes showed distinct trends with depth; while the POC flux slightly decreased from below the upper oxycline (60 m) to 180 m, the PN flux slightly increased with depth. On the other hand, the fluxes of POP, BSi, Chl *a* and TEP showed a distinctive peak in the core of the OMZ (at 110 m). In the LD, the POC flux decreased in the fully oxygenated upper water column (between 40 and 55 m), and remained relatively constant in the OMZ (between 60 and 180 m); PN flux, steadily~~,~~

decreased with depth. Similar to GB, but smaller, a peak of POP, BSi, Chl *a* and TEP fluxes was observed at 110 m. This high flux of POM at 110 m in both stations coincided with the appearance of dark, star-shaped particles, particularly evident at GB (Fig. 6a, e), but also present in LD, which may correspond to MnOx particles enriched in OM that have been described in the GB and the LD before (Neretin et al., 2003; Pohl et al., 2004). Similar to the vertical distribution on POM in the water column discussed in the section above, differences in POM fluxes between stations are likely associated with the large inflow of oxygen-rich saltwater that displaced the old, stagnant water masses and changed the chemistry of the water column (Myllykangas et al., 2017). Under euxinic (*e.i.*, no MBI) conditions, the maximum concentration of particulate Mn is found at the depth of the oxycline (Glockzin et al., 2014). Below the oxycline, and due to the hydrogen sulfide (H_2O) presence, the particulate Mn concentration decreased drastically. During this study, we observed high concentration of MnOx particles flux at 110 and 180 m (Table 5) in the GB; this result agreed with the high flux of particulate Mn measured in sediment traps located at 186 m in June 2015 (Dellwig et al., 2018). The oxygenation of the deep water layers of the GB by the MBI caused the absence of H_2S (Schmale et al., 2016) and provided the redox conditions to measured high MnOx flux in the sediment trap located in the core of the OMZ (110 m) and at 180 m. There were two possible sources of MnOx in the GB associated with the 2014/2015 MBI, on one hand, the lateral transport of low-density aggregates formed by MnOx and OM (Glockzin et al., 2014), and on the other hand, the remarkable *in-situ* formation and deposition of MnOx from dissolved Mn, which inventory drastically decreased in the water column due to the change in redox conditions (Dellwig et al., 2018). In clear contrast to the oxygenated deep layers of the GB, in the LD, we measured H_2S at 180 m, this could explain why although those aggregates were present in this station below the oxycline (*i.e.,* 70 m) at 110 m, they dissolved in sulfidic waters, thus were not as abundant, and did not form aggregates with TEP (Fig.6c).

The presence of MnOx-containing aggregates enriched in OM (see TEP fluxes, Fig 6c) may have implications for the vertical flux of C and N in a stratified system with a pelagic redoxcline like the Baltic Sea. Under steady state, the upward diffusion and oxidation rate of the dissolved Mn

are balanced by the sinking and dissolution rate of MnOx. During the Mn-oxidation, the POM could aggregate with the MnOx including particulate elements, and trace metals. Then, in the sulfidic waters, slow-sinking MnOx enriched in OM will be dissolved liberating the OM and altering the vertical distribution and the flux of all associated particle elements (Glockzin et al., 2014). For example, in the Cariaco Basin, total particulate phosphorus reached their maximum flux in sediment traps close to the redoxcline (Benitez-Nelson et al., 2004; Benitez-Nelson et al., 2007). MnOx formation and scavenging of trace metal may be a relevant mechanism for transfer trace metals from the oxygenated to the anoxic deep waters (Dellwig et al., 2010). Moreover, even in the anoxic zone, the abundant aggregate associated bacteria (Grossart et al., 2006) could partially or completely degrade the organic compounds in those particles using NO_3^- or MnOx as an electron acceptor. This may explain why we observed a clear peak in the flux of POP, BSi, Chl a (Fig. 3a, b), TEP (Fig. 6a) and TCHO (Fig. 7a) at 110 m followed by a small decrease at 180 m in the GB. In the LD a smaller increment in the flux of POP, BSi (Fig. 3d), TEP (Fig. 6c) and TCHO (Fig. 7b) was also observed. The vertical fluxes of those compounds coincided with the abundance of MnOx particles; we assume that the MnOx aggregated not only with TEP as described before (Glockzin et al. 2014) and observed in this study (Fig. 6a) but also with POP, BSi, Chl *a*, and TCHO. On the other hand, nitrogen-rich components of POM like PN (Fig. 3a), TAA (Fig. 7a), and CSP (Fig. 6a) gradually decreased with depth in the GB, suggesting that those compounds were less scavenge by MnOx-OM rich aggregates.

Primary production (PP) in the GB was 10% higher than in LD during our study (Piontek et al. unpublished data). However, the POC flux below the euphotic zone (at 40 m) was 42% higher in LD than in GB and comparable at both stations at 180 m. The fraction of PP exported as POC is termed export production (*e-ratio*) (Buesseler et al., 1992), and it is calculated as the POC flux below the euphotic zone divided by the primary production. The *e-ratio* was calculated here using the ^{14}C based PP (Piontek et al. unpublished data) and carbon flux at 40 m (shallowest sediment trap depth, considered at the base of the euphotic zone). The *e-ratio* was 0.41 in the GB and 0.77 in the LD*; i.e.*, in GB 41% of the primary production was exported as POC below the euphotic

zone (40 m) versus 77% in the LD. This suggests that a higher proportion of the primary production was remineralized in the euphotic zone of the GB compared with the LD. On the other hand, the transfer efficiency of POC to the deeper water column (*i.e.* the ratio of POC flux at180 m over POC flux at 40 m) was higher in the GB (115%) than in the LD (69%). The transfer efficiency of POM is largely controlled by the remineralization rate and the sinking velocity of particles (De La Rocha and Passow, 2007; McDonnell et al., 2015; Trull et al., 2008). The higher POC transfer efficiency in the GB than in the LD can be attributable to differences in the sinking velocities of the particles in those two stations. Particulate MnOx may sink through the redoxcline in the GB (Neretin et al., 2003) acting as ballast material and nucleus for MnOx-OM rich aggregates formation. Those aggregates could have sunk more quickly, limiting the time spent in the water column and the degradation by particle- attached microbes. Assuming that MnOx had a density between 1.5 and 2.0 g cm^{-3} (Glockzin et al., 2014). The largest particles measured in GB (167 μm, Table 4) will have a sinking velocity based in Stokes' law between 508 and 1014 m d^{-1}. If we considered a mixed aggregate that is 50% TEP, density 0.9 g cm^{-3} (Azetsu-Scott and Passow, 2004) and 50% MnOx (density 1.5 g cm^{-3}), its density would be 1.2 g cm^{-3}, and its theoretical sinking velocity will be 204 m d^{-1}. This indicates that theoretically, the largest mix aggregates composed of MnOx and TEP observed in the GB could reach 180 m (the location of our deepest sediment trap) in less than one day. However, the average measured sinking velocity of MnOx in the laboratory for particles between 2 and 20 μm was 0.76 m d^{-1}, this is significantly lower than the theoretical value (Glockzin et al., 2014). Glockzin et al. (2014) suggested that the star shape and the content of OM were responsible for the lower than predicted sinking velocity. There is no information about the amount of OM relatively to MnOx particles in those mix aggregates, or how the MnOx to OM ratio may affect the density and sinking velocity of larger aggregates like the ones we observed. Due to the shape and size of MnOx-OM aggregates observed in our study (Fig. 6e), we could assume those are the same type of aggregates described before by Glockzin et al. (2014). Although we did not measure the sinking velocity of those aggregates, we did observe a higher abundance of them associated with TEP at 110 and 180 m in

604 the GB than in the LD. The formation of these organic matter rich MnOx aggregates could
605 represent an additional mechanism (see introduction) to explain why the efficiency of the OM
606 export is different under anoxic that under oxic conditions in the Baltic Sea. The oxygenation of
607 anoxic deep water in the GB caused by the 2014/2015 MBI, may have led to an enhanced
608 precipitation of manganese, iron and phosphorus particles (Dellwig et al., 2010; Dellwig et al.,
609 2018). For example, the formation of P-rich, metal oxides precipitates occur in the anoxic waters
610 of the Black Sea (Shaffer, 1986) and Cariaco Basin (Benitez-Nelson et al., 2004; Benitez-Nelson
611 et al., 2007) were higher concentration of particulate inorganic and organic phosphorus have been
612 observed in sediment traps close to the redoxcline.

613 *4.3 Differences on composition and lability of sinking and suspended organic matter in the GB*
614 *and the LD*

615 In the sections above, we discussed how similar were biogeochemical conditions and the size of
616 the surface POM pool in both the GB and the LD. We then looked at how the sinking flux of OM
617 was affected by the different O_2 concentrations in the water column. We now focus on the
618 influence of O_2 in the chemical composition of sinking and suspended POM. Suspended or slow
619 sinking POM, that spend more time in the water column, should theoretically, show a larger
620 degree of degradation (Goutx et al., 2007). Relative to the Redfield molar ratio: 106 POC:16
621 PN:POP, OM showed an enrichment in carbon, especially in sinking particles from the LD and
622 suspended OM from the GB (Table 5). Our measured values of POC:PN (~10) and POC:POP
623 (between 89 and 506) in suspended OM coincide with the simulated ratio reported by Kreus et al.
624 (2015) immediately after the culmination of the spring bloom, those relatively high ratios are
625 consequence of the nitrogen depletion and are characteristic during the summer in the Baltic Sea.
626 The same study had suggested that POC:POP higher than Redfield ratio might lead to an
627 enhancement of particle export (Kreus et al., 2015), however, no direct observations had
628 confirmed this hypothesis. Our measurements showed that the relative higher POC:POP ratios in
629 sinking OM from LD, compared with the GB, do not lead to a higher transfer efficiency at this

station. Compared to the suspended OM in the LD, the POP content was lower in the GB, possible related to scavenging of POP into MnOx aggregates (see section 3.4).

The TAA based degradation index, DI (Dauwe et al. 1999) covers a wide range of alteration stages; the more negative the DI, the more degraded the samples, positive DI indicates fresh organic matter. In our study, the sediment trap material had a DI between 0.10 and 1.14, while suspended OM has a DI between -0.26 and -1.25 (Table 4). These values coincide with what reported earlier by Dauwe et al. (1999), and indicate that: first, the sinking particles collected in the sediment traps were less altered (they have a more positive DI) than the suspended OM collected in the Niskin bottle. Second, sinking particles from the GB were fresher than the ones from the LD, and the degradation stage increased with depth in both stations. The higher contribution of AA and CHO to the POC pool in sinking than in suspended OM and the AA- DI indicates that suspended OM was more degraded than sinking OM. The highest degree of degradation in suspended OM and sinking OM from the LD may be the result of a long time that light suspended OM or slow sinking particles spend exposed to degradation in fully oxygenated surface waters than dense, fast sinking particles collected in sediment traps.

The higher abundance of aggregates, formed by a combination of MnOx-like particles and OM, observed at 110 and 180 m in the GB could act as bacteria hot spots that combined with a higher O_2 concentration in the GB may increase the microbial degradation on sinking particles collected in the GB. However, the AA-DI, indicated that sinking OM was less altered and therefore more labile than the sinking OM in the LD. This implied that in addition to the higher transfer efficiency of POC in the GB (see discussion above); the OM reaching the seafloor was fresher and less degraded. This supports the idea that mix aggregates composed by MnOx and OM may be larger and faster sinking than the previously described by Glockzin et al. (2014). This explanation is mostly speculative, and based on the observation of large mixed aggregates in the 110 and 180 m traps (Fig. 6, Table 4). However, as mention in the previous section, further work on directly determines sinking velocity is required to prove this hypothesis.

Conclusion

Fluxes and composition of sinking particles were different in two deep basins in the Baltic Sea: the GB and the LD during early summer 2015. The two stations had similar surface characteristics and POM stock; however, at depth, the vertical profile of the O_2 concentration was different. The 2014/2015 MBI supplied oxygen-rich waters to the GB transporting solid material from the and modifying the O_2 vertical profile and the redox conditions in the otherwise permanent suboxic deep waters. This event did not affect the LD allowing the comparing POM fluxes and composition under two different O_2 concentrations with similar surface water conditions. Export efficiency (*e-ratio*) derived from *in-situ* PP measurements and POC flux derivate from sediment traps indicated higher export efficiency in LD than in GB. However, the transfer efficiency (POC flux at 180 m over POC flux at 40 m) suggested that under anoxic conditions found in the LD, a smaller portion of the POC exported below the euphotic zone was transferred to 180 m than under re-oxygenated conditions present in the GB. The 2014/2015 MBI also transport solid Mn from shallower areas towards the GB deep that may have contributed to the higher abundance of MnOx-OM in the GB. Our results suggest that a new possible mechanism to explain the differences in the OM fluxes under different O_2 concentration could be the formation and prevalence of aggregates composed of MnOx and organic matter in the GB. Those aggregates were significantly larger and more abundant in the GB compared to the LD where sulfidic waters constrained their presence. We propose that after a MBI in the GB, the aggregates containing MnOx-like particles and organic matter could have reached the sediments relatively fast and unaltered, scavenging not only phosphorus and TEP, as described previously, but also other organic compounds. The remineralization of this organic matter reaching the sediments may contribute to the quick re-establishment of anoxic conditions in the sediment-water interface in the GB. The relevance of this process needs to be further investigated in order to be included in O_2 budget and long-term predictions of the MBI impact in the O_2 and OM cycles.

Author Contributions

C.C.N. performed deployments, analyzed samples and wrote the manuscript. F.A.C.L.M, performed deployments and contributed to the writing of the manuscript. A.E designed and conducted the scientific program at sea and discussed and commented on the manuscript.

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Figure Captions

Figure 1. Monthly averaged Chl *a* distribution derived from VIIRS for June 2015 in the Baltic Sea. Black circle and "x" indicate the position of the trap deployment and the seawater collection respectively in Gotland Deep (GB) and Landsort Deep (LD). The lower panel shows the trajectory of the trap deployed at GB and LD.

Figure 2. Water column profiles at the location of the sediment trap deployments in (A) the GB, and (B) the LD. Left panel: oxygen (blue), temperature (red), and salinity (black). Middle panel: nitrate (NO_3), nitrite (NO_2), and ammonium (NH_4). Right panel: phosphate (PO_4), and silicate ($Si(OH)_4$). Grey lines indicate the depths at which we deployed sediment traps.

Figure 3. Particulate organic matter profiles in the water column at the location of the sediment traps deployments in the GB (A, B and C) and the LD (D, E and F). (A and D) particulate organic carbon (POC), particulate nitrogen (PN), and particulate organic phosphorous (POP). (B and E) chlorophyll a (Chl a) and biogenic silicate (BSi). (C and F) transparent exopolymeric particles (TEP) and Coomassie stainable particles (CSP). Grey lines as figure 2.

Figure 4. MnOx-like containing particles and O_2 concentration profiles in the water column at the location of the sediment traps deployments. (A) the GB and (B) the LD. Grey lines as in figure 3.

Figure 5. Particulate organic matter fluxes in the GB (A and B) and the LD (C and D) . (A and C) POC, PN and O_2. (B and D) POP, Chl a, and BSi.

Figure 6. TEP and CSP fluxes in the GB (A and B) and the LD (C and D). In addition to the vertical distribution of the flux, each profile is complemented with images captured under the microscope (200x) at each depth. Star-shaped MnOx-like particles are clearly visible in the GB associated to TEP (A), but not with CSP (B). MnOx-like particles were significantly less abundant in the LD (C and D). (F) A larger magnification (400x) image of MnOx-like particles at 110 m showing more detail on the shape of those particles and aggregates formed with TEP.

Figure 7. Total hydrolyzable amino acids (TAA) and total carohydrates (TCHO) fluxes in (A) the GB, and (B) the LD.

Table 1. Sediment traps deployment and recovery locations, dates, collection times and depths.

Station	Lat	Lon	Date	Station depth	Deployment time (d)	Trap depths (m)
Gotland Basin (GB)	57.21 °N	20.03 °E	08/06/2015	248 m	2	40A, 40B, 60, 110, and 180m
	57.27 °N	20.25 °E	10/06/2015			
Landsort Deep (LD)	58.69 °N	18.55 °E	15/06/2015	460 m	1	40A, 40B, 55, 110, and 180m
	58.68 °N	18.68 °E	16/06/2015			

Table 2. Abundance of chlorophyll and phycoerythrin containing pico- and nanoplankton measured by flow-cytometry in the GB and the LD.

	Depth (m)	Phytoplankton (cells mL^{-1})			Cyanobacteria-like (cells mL^{-1})		
		picoplankton	nanoplankton	Total	picoplankton	nanoplankton	Total
GB	1	87963	2097	90060	5225	731	5956
	10	94369	2628	96997	8795	920	9716
	40	4999	68	5067	2174	69	2243
	60	4125	35	4160	1990	42	2032
	80	599	7	606	238	15	253
	110	594	7	601	326	29	356
	140	1144	14	1158	356	2	358
	180	908	9	917	366	20	385
	220	2270	19	2289	1063	34	1097
LD	1	92359	2283	94642	834	177	1011
	10	86426	1708	88134	2990	232	3223
	40	2022	92	2114	2243	69	2312
	60	1524	62	1586	1294	24	1318
	70	908	43	951	613	17	630
	110	1735	82	1817	1181	17	1198
	180	1339	75	1415	946	34	980
	250	1593	82	1676	949	36	985
	300	1521	48	1569	1047	17	1064
	350	1608	57	1665	908	12	920
	400	1548	73	1621	1047	22	1069
	430	1562	68	1631	875	19	894

Table 3. Phytoplankton abundances analyzed microscopically in the GB and the LD, volume analyzed was 50 ml per sample.

		GB (cells mL^{-1})				LD (cells mL-1)			
		1 m	10 m	40 m	Total	1 m	10 m	40 m	Total
Cyanophyceae *	Total	14148	13536	0	27684	37368	32526	96	69990
Chryptophyta	Total	140	112	28	280	1400	882	56	2338
Bacillariophyceae	Total	96	94	44	234	462	112	102	676
	Chaetoceros sp.	58	42	24	124	434	106	26	566
	Skeletonema sp.	26	8	12	46	12	0	8	20
	Thalassiosira sp.	12	44	8	64	16	6	68	90
Dinophyceae	Total	3772	4424	1192	9388	9032	7662	1404	18098
	Dinophysis sp.	678	742	2	1422	450	214	4	668
	other	3094	3682	1190	7966	8582	7448	1400	17430
Chlorophyta	Total	5320	6860	28	12208	2072	1022	238	3332
	Planctonema sp.	5320	6860	28	12208	2072	1022	238	3332

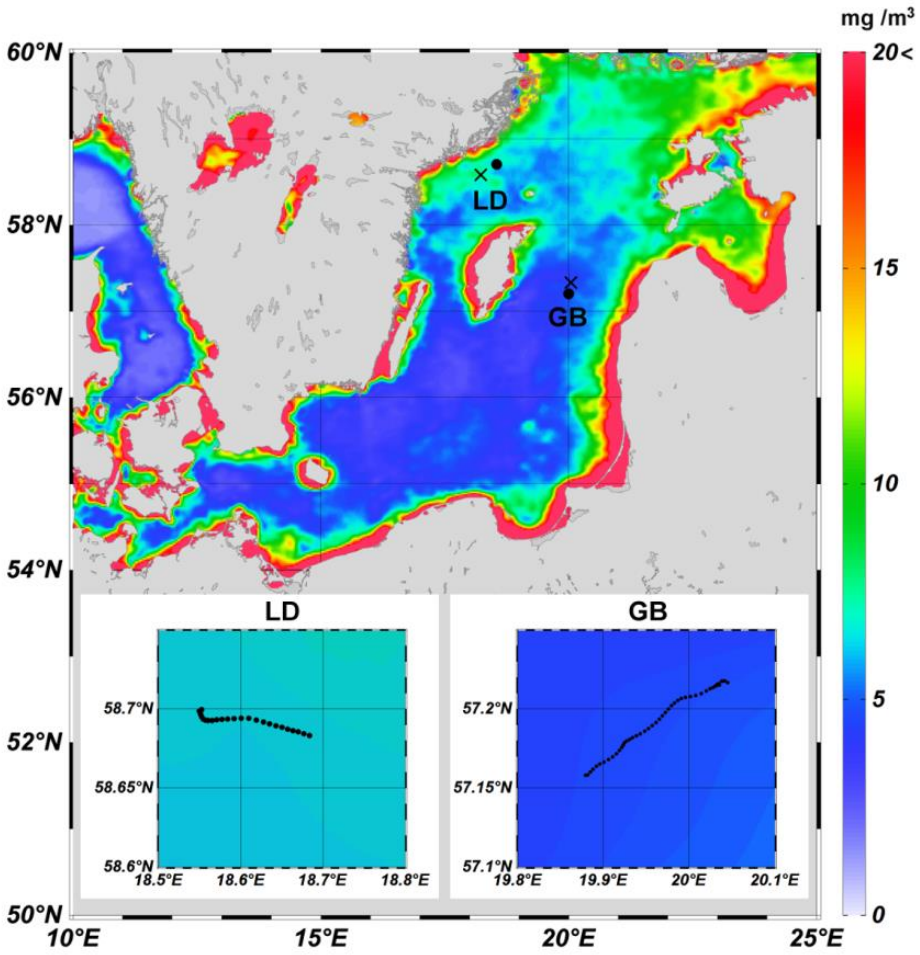
* >90% were filamentous cyanobacteria *Aphanizomenon* sp.

Table 4. MnOx-like particles fluxes and size determined by image analysis in GB -and LD.

Station	Depth (m)	MnOx-like particles ($cm^2\ m^{-2}d^{-1}$)	Median size ESD (μm)	Size range ESD (μm)
GB	110	5666.1± 993.5	2.8	0.6-166.7
	180	7789.1± 954.7	3.3	0.6-152.7
LD	110	50.3±1.8	1.8	0.6-16.5
	180	2.6±0.3	1.4	1.2-9.3

Table 5. Amino acids (AA), carbohydrates (CHO) and elemental molar ratios of sinking and suspended OM in the GB and in the LD.

	Depth (m)	AA-C:POC %	CHO-C:POC %	POC:PN	POC:POP	POC:Bsi	PN:POP
GB	40	19.19	18.26	9.80	244.05	3.86	0.39
sinking OM	40	17.58	17.21	9.43	222.42	4.07	0.43
	60	15.78	17.56	9.52	231.56	2.78	0.29
	110	13.87	22.24	11.31	90.12	1.73	0.15
	180	11.13	18.47	12.68	122.87	2.97	0.23
LD	40	13.52	9.43	12.17	771.70	3.58	0.29
sinking OM	40	14.27	8.40	11.09	413.14	4.12	0.37
	55	19.10	10.97	12.43	331.81	3.03	0.24
	110	13.37	11.97	15.44	229.70	2.67	0.17
	180	14.32	12.85	15.29	341.33	4.19	0.27
GB	1	8.22	16.94	10.39	154.56	91.45	14.88
suspended							
OM	10	10.81	8.84	10.48	150.51	87.15	14.36
	40	4.91	2.80	9.19	88.78	133.75	9.66
	60	5.43	2.66	9.78	127.36	125.24	13.02
	80	4.67		10.43	144.92		13.89
	110	9.01	6.63	8.45	245.26		29.01
	140	5.34		10.60	283.42		26.73
	180	5.73	4.29	11.37	506.21		44.54
	220	8.57	3.35	12.06	270.78		22.45
LD	1	6.96		8.66	205.29	514.94	23.71
suspended							
OM	10	12.97	9.12	8.43	196.44	100.91	23.31
	40	0.00	8.88	8.09	335.66	24.48	41.51
	60	6.09	10.26	7.83	300.75	16.89	38.43
	70	7.92	10.72	7.71	291.81	247.80	37.86
	110	12.22	5.41	7.93	224.56		28.32
	180	10.12	11.32	7.02	205.33		29.23
	250	11.97	8.81	6.52	249.36		38.22
	300	10.88		6.71	136.67		20.37
	350	10.67	10.12	6.76	145.80		21.56
	400	9.99		6.18	229.53		37.16
	430	9.35	9.45	7.82	148.61		19.01


mg /m3
20<
15
10
5
0
60°N
58°N
56°N
54°N
52°N
50°N
10°E
15°E
20°E
25°E
LD
GB
LD
GB
58.7°N
58.65°N
58.6°N
18.5°E
18.6°E
18.7°E
18.8°E
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57.15°N
57.1°N
19.8°E
19.9°E
20°E
20.1°E

Fig. 1

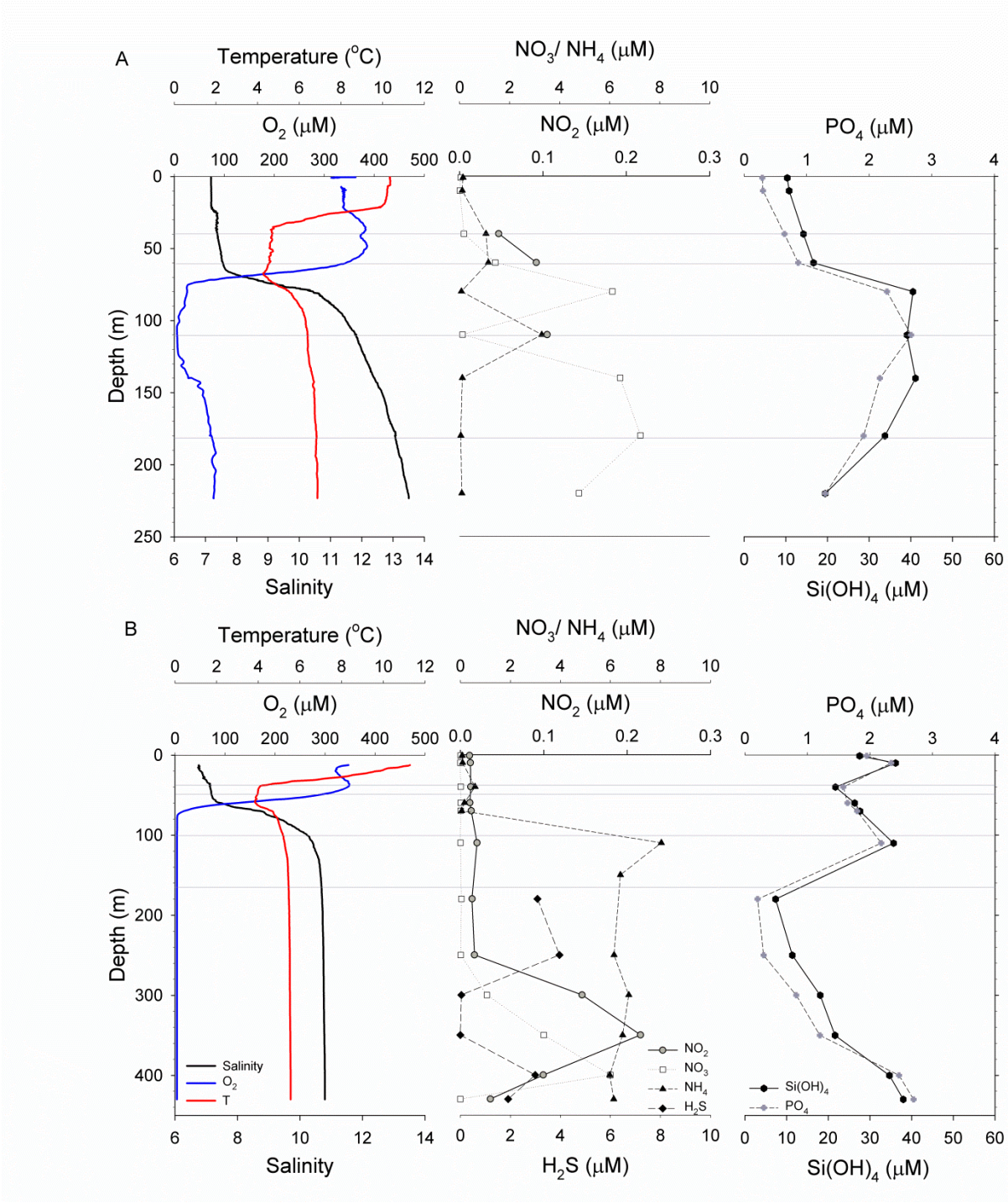
A
Temperature (°C)
NO_3/ NH_4 (μM)
O_2 (μM)
NO_2 (μM)
PO_4 (μM)
Depth (m)
Salinity
$Si(OH)_4$ (μM)
B
Temperature (°C)
NO_3/ NH_4 (μM)
O_2 (μM)
NO_2 (μM)
PO_4 (μM)
Depth (m)
Salinity
O_2
T
NO_2
NO_3
NH_4
H_2S
Si(OH)4
PO_4
Salinity
H_2S (μM)
$Si(OH)_4$ (μM)

Fig. 2

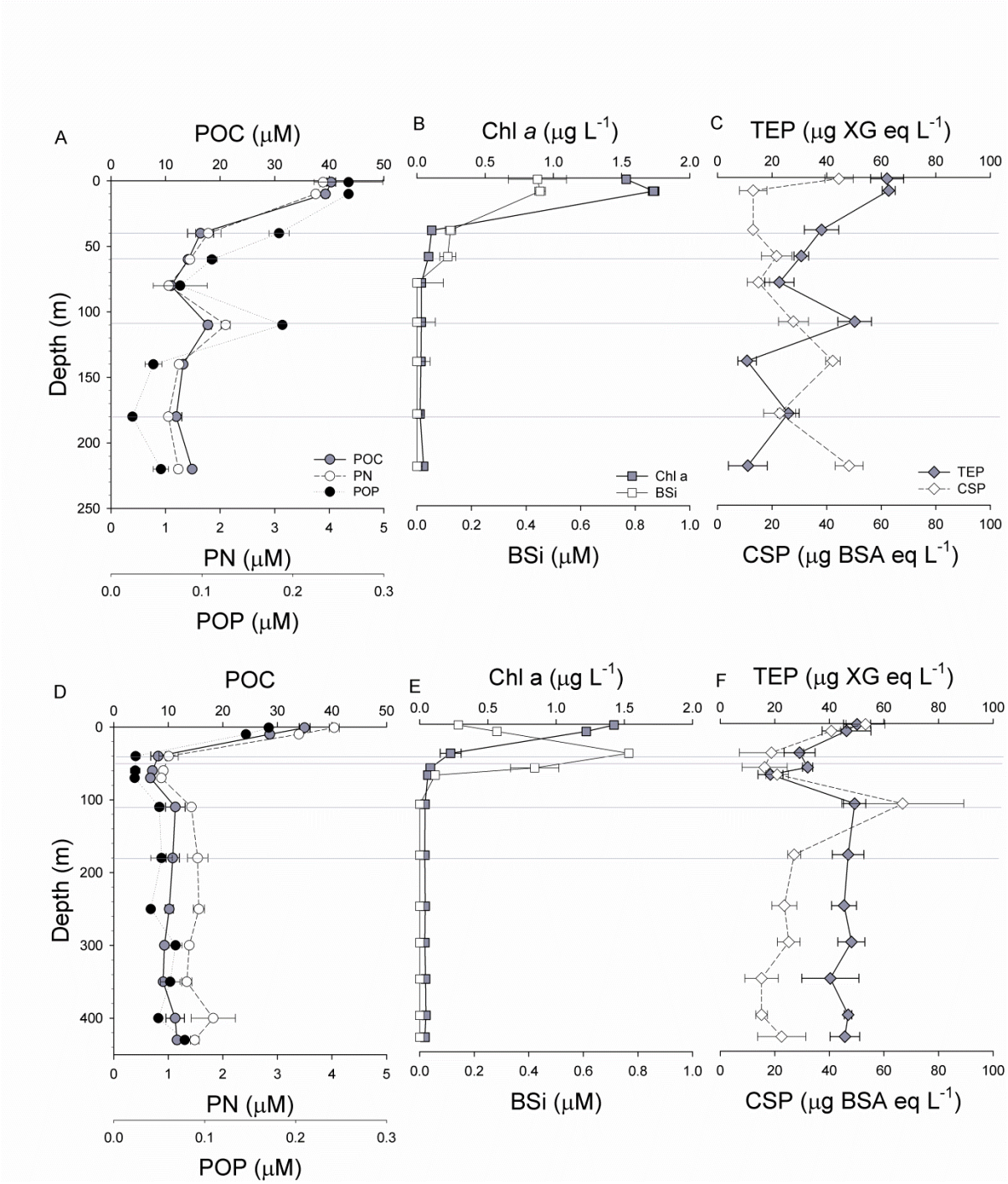
A
POC (μM)
B
Chl *a* (μg L^{-1})
C
TEP (μg XG eq L^{-1})
Depth (m)
POC
PN
POP
Chl a
BSi
TEP
CSP
PN (μM)
POP (μM)
BSi (μM)
CSP (μg BSA eq L^{-1})
D
POC
E
Chl a (μg L^{-1})
F
TEP (μg XG eq L^{-1})
Depth (m)
PN (μM)
POP (μM)
BSi (μM)
CSP (μg BSA eq L^{-1})

Fig. 3

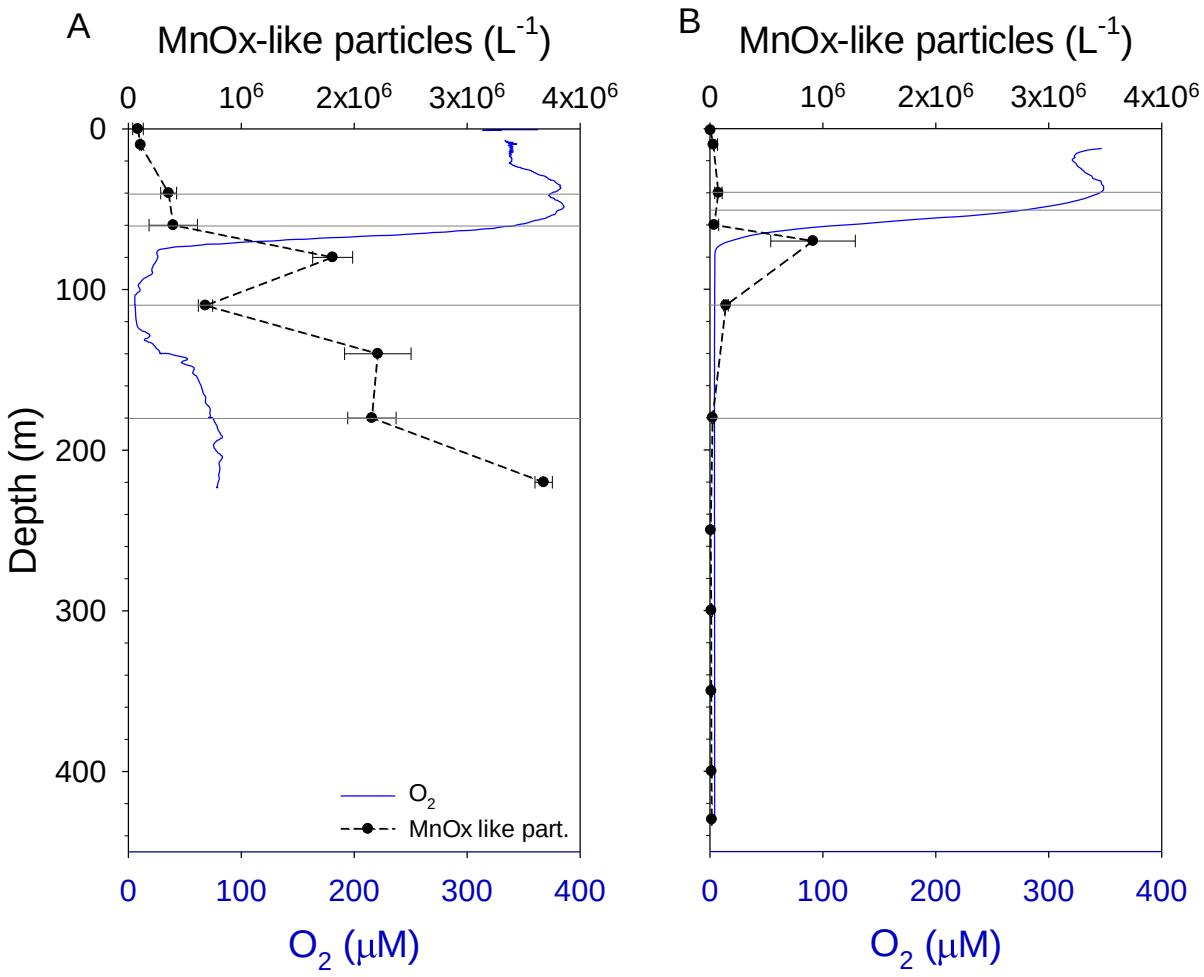
A
MnOx-like particles (L-1)
0
10^6
2x10^6
3x10^6
4x10^6
Depth (m)
0
100
200
300
400
O2
MnOx like part.
0
100
200
300
400
O2 (µM)
B
MnOx-like particles (L-1)
0
10^6
2x10^6
3x10^6
4x10^6
0
100
200
300
400
O2 (µM)

Fig. 4

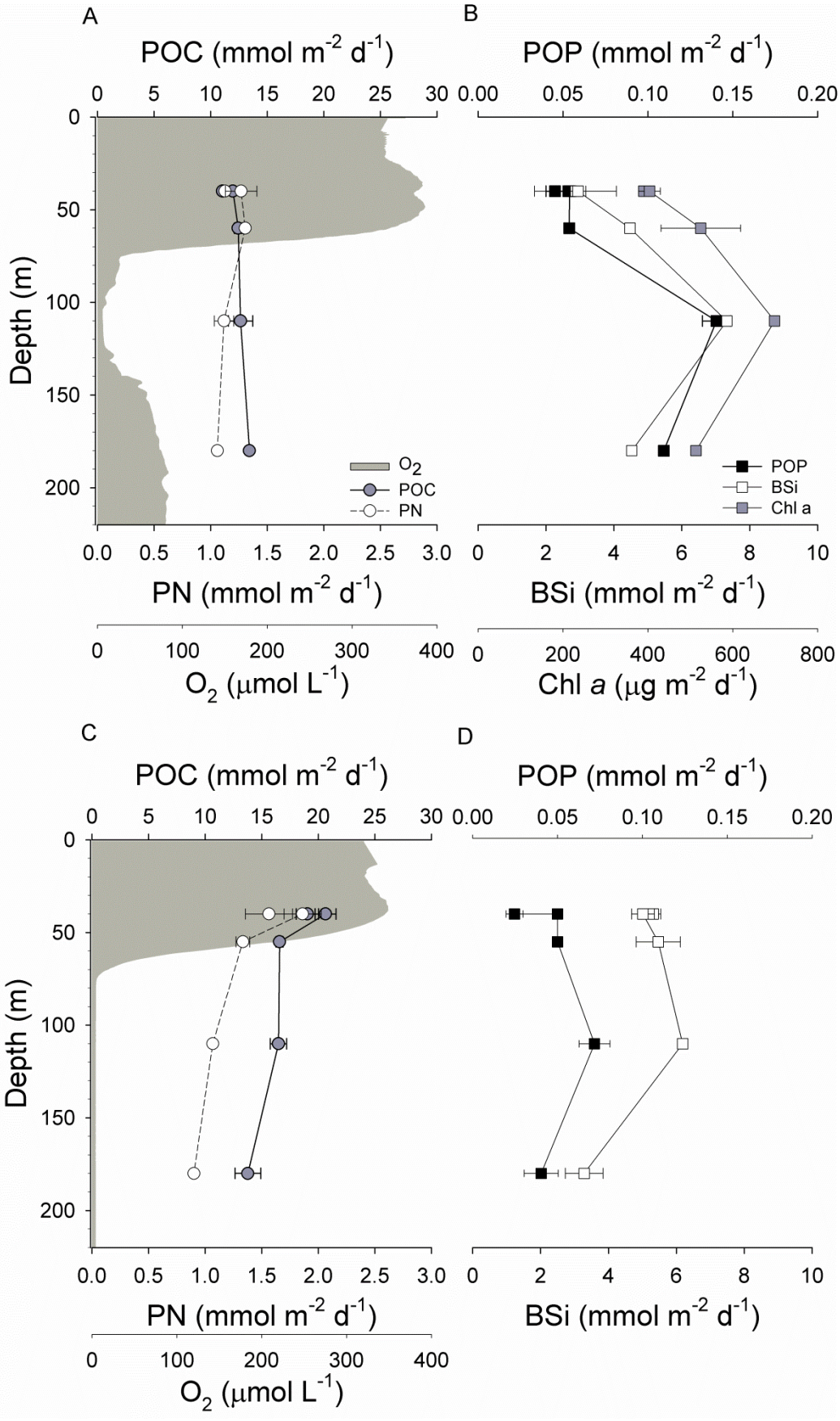
A
POC (mmol m-2 d-1)
0 5 10 15 20 25 30
Depth (m)
0 50 100 150 200
O2
POC
PN
0.0 0.5 1.0 1.5 2.0 2.5 3.0
PN (mmol m-2 d-1)
0 100 200 300 400
O2 (µmol L-1)
B
POP (mmol m-2 d-1)
0.00 0.05 0.10 0.15 0.20
POP
BSi
Chl a
0 2 4 6 8 10
BSi (mmol m-2 d-1)
0 200 400 600 800
Chl a (µg m-2 d-1)
C
POC (mmol m-2 d-1)
0 5 10 15 20 25 30
Depth (m)
0 50 100 150 200
0.0 0.5 1.0 1.5 2.0 2.5 3.0
PN (mmol m-2 d-1)
0 100 200 300 400
O2 (µmol L-1)
D
POP (mmol m-2 d-1)
0.00 0.05 0.10 0.15 0.20
0 2 4 6 8 10
BSi (mmol m-2 d-1)

Fig. 5

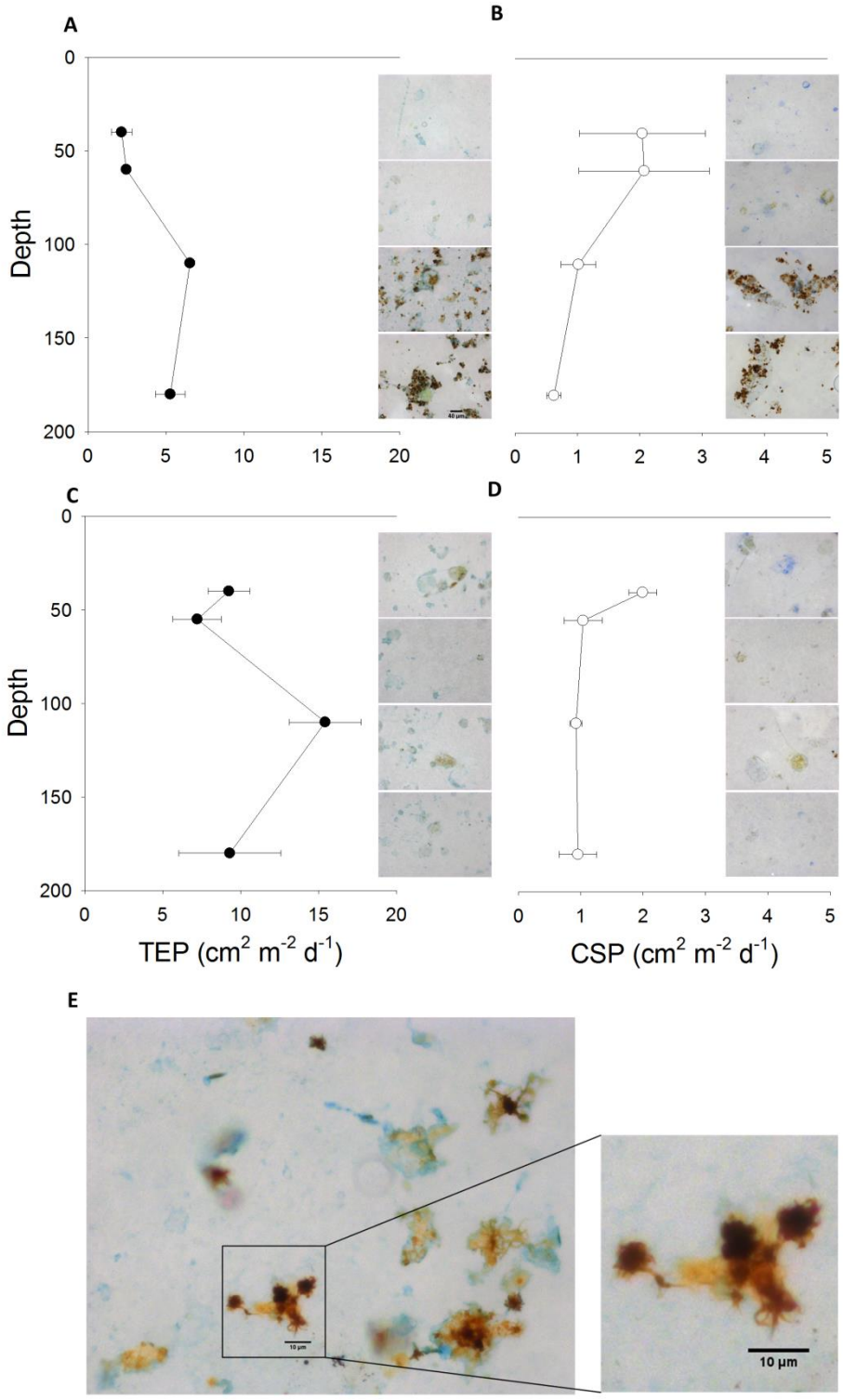
A
B
C
D
E
Depth
0
50
100
150
200
0
5
10
15
20
1
2
3
4
TEP (cm^2 m^{-2} d^{-1})
CSP (cm^2 m^{-2} d^{-1})
10 µm

Fig. 6

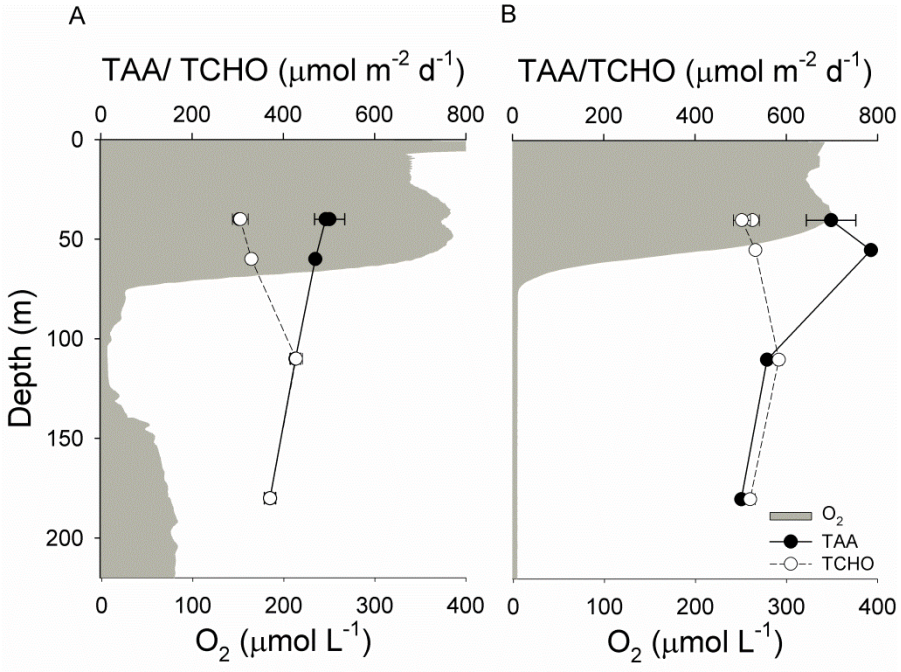
A
B
TAA/ TCHO (μmol m-2 d-1)
TAA/TCHO (μmol m-2 d-1)
0
200
400
600
800
Depth (m)
0
50
100
150
200
0
100
200
300
400
O2 (μmol L-1)
O2
TAA
TCHO

Fig. 7